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WILFRED R. McLEOD

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APPLICATIONS OF MOLECULAR REFRACTION

TO THE PRINCIPLE OF CORRESPONDING STATES

APPROVED BY

J. A. Campbell

D. E. Menzie

F. M. Townsend

Arthur Burnhart

John A. E. Northon

DISSERTATION COMMITTEE

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CHAPTER I

THE PROBLEM

Although extensive progress has been made in the development of equations of state to predict the behavior of pure components, there remains yet a dire need for improvement in the prediction and correlation of the volumetric behavior of fluid mixtures.

To the petroleum reservoir engineer making volumetric predictions for evaluation purposes or the natural gas engineer involved in estimating fluid properties for design purposes, the need for a reliable predictive and correlative method becomes more acute as he deals with more and more complex mixtures at elevated temperatures and pressures.

At present, the physicochemical concept of corresponding states remains the industry's most useful predictive and correlative approach in dealing with these fluid systems. This approach could be called satisfactory in the sense that the results are useful. Unfortunately, the most precise approaches are tedious and have too high a degree of uncertainty for many complex mixtures.

Many past investigators have done much to increase the accuracy of this concept by introducing "third parameters". Two of these most accepted correctors are Meissner and Seferian's Z_c, critical compressibility factor, and Pitzer's ω, acentric factor.

These two improvements have had a fair amount of success in dealing with light hydrocarbon systems. However, their common failings, along with all other existing third parameters, are:

1. Their high degree of inaccuracy in dealing with hydrocarbon fluid systems containing varying amounts of any or all of the following nonhydrocarbon compounds, i.e., helium, carbon dioxide, nitrogen and hydrogen sulfide.
2. Failure to adequately characterize the heptanes plus fractions in systems containing the same.

This study will first provide a third parameter, Eykman Molecular Refraction (EMR). With this modified approach to the corresponding states concept, new gas compressibility, liquid density, and fluid viscosities correlations will be presented.

CHAPTER II

EQUATION OF STATE FOR GASEOUS SYSTEMS

The literature contains numerous equations of state of which only three will be discussed in this chapter. The reader will find adequate discussions on other equations in the independent studies of Sarem (104), Satter (105), and Buxton (11).

A. The Ideal Gas Law

All fluids follow different equations of state. For a pure gas the mathematical representation is as follows:

$$f\ (P,\ V,\ T) = 0 \tag{2-1}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \tag{2-2}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T\ =\ T_c} = 0 \tag{2-3}$$

Figure (2-1) is a pictorial representation of the above equations. The simplest form of the equation of state is the familiar ideal gas law, i.e.:

$$PV = RT \tag{2-1a}$$

B. Semi-Empirical Equations of State

Historically the most celebrated equation of state is that of van der Waal. It is the earliest known attempt to take into consideration the effect of molecular volume and intermolecular forces. The equation in its simplest form (for one mole of gas) is:

$$\left(P + \frac{a}{V^2}\right)\left(V-b\right) = RT \tag{2-4}$$

where a = intermolecular force correction constant

b = molecular volume correction constant

The constants a and b, supposedly independent of temperature and pressure, must nevertheless be evaluated for each fluid under consideration. Combinations of equations (2-1), (2-2), and (2-3) are used for the evaluation of the constants.

$$\left(\frac{\partial P}{\partial V}\right)_{T = T_c} = \frac{2a}{V_c^3} - \frac{RT_c}{(V_c-b)^2} = 0 \tag{2-5}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T = T_c} = \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0 \tag{2-6}$$

from which

$$a = \frac{RT_cV_c}{8} \tag{2-7}$$

$$b = \frac{V_c}{3} \tag{2-8}$$

and $$R = \frac{8}{3}\,\frac{P_cV_c}{T_c} \tag{2-9}$$

Inasmuch as the reliability of critical volume (V_c) measurements is more

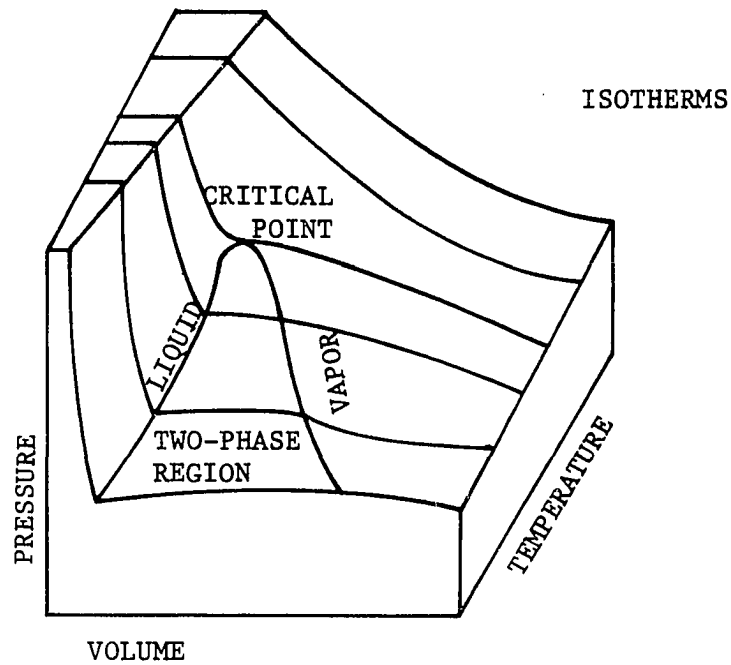


FIGURE 2-1. PICTORIAL REPRESENTATION OF THE EQUATION OF STATE

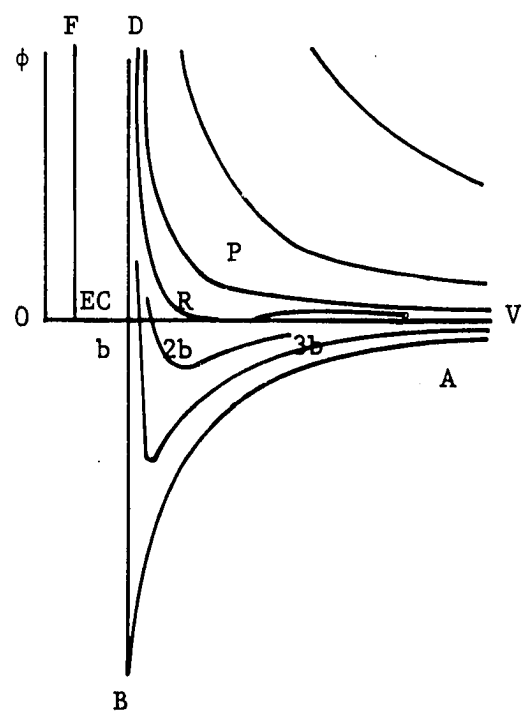


FIGURE 2-2. PICTORIAL REPRESENTATION OF A TYPICAL VAN DER WAAL'S GAS

questionable than either critical pressure or critical temperature, equations (2-4, (2-7), and (2-8) can be combined to give:

$$a = \frac{27\ R^2 T_c^{\ 2}}{64\ P_c} \tag{2-10}$$

$$b = \frac{RT_c}{8P_c} \tag{2-11}$$

Figure 2-2 is a system of isothermal curves of a real gas as represented by van der Waal's equation. The line AB is the curve $P = -a/V^2$, and BCD is the curve V= b. The isothermal lines show that below a certain temperature P goes through a maximum, a minimum, and then increases again as V decreases. In the upper right hand quadrant, at high temperatures, the curves assume the shape of rectangular hyperbolas as in the case of the ideal gas.

Considerations of van der Waal's equation have revealed that a and b are functions of temperature and pressure instead of mere constants. It has been suggested that at higher temperatures, the violence of the impact on collisions between the molecules might be expected to cause a deformation of molecular structure, altering the value of a. Furthermore, at high temperatures and pressure actual compression of the molecules themselves would lead to the value of b being altered.

Two of the earliest attempts to improve on the van der Waal equation resulted in the following equations:

$$P = \left(\frac{RT}{V-b}\right) e^{-\frac{a}{VRT}} \qquad \text{(Dieterici equation)} \tag{2-12}$$

$$a' = \frac{RT_c}{P_c e^2} \tag{2-13}$$

$$b' = \frac{RT_c}{P_c e^2} \tag{2-14}$$

and $$P = \frac{RT}{V-b'} - \frac{a''}{TV^2} \quad \text{(Berthelot equation)} \tag{2-15}$$

$$a'' = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \tag{2-16}$$

$$b'' = \frac{RT_c}{8P_c} \tag{2-17}$$

C. Empirical Equations of State. Virial Coefficients

In this approach the equation of state is expressed in the form of a power series in terms of density or pressure, i.e.:

$$PV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^4} + \ldots\ldots\right) \tag{2-18}$$

or

$$PV = RT + B'P + C'P^2 + D'P^4 + \ldots \tag{2-19}$$

where B, C, ..., B', C' ... are functions of temperature and are called, respectively, the second, third and fourth virial coefficients.

The most established method for evaluating the second virial coefficients for simple non-polar spherical molecules utilizes the Lennard-Jones potential function (see Figure 2-3).

$$U(r) = 4\hat{\varepsilon} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{2-20}$$

where: $U(r)$ = the intermolecular potential function

$\hat{\epsilon}$ = the magnitude of the potential energy minimum

σ = the collision diameter for low velocity collision between two molecules

r = distance of separation of the molecules

Equation (2-20) shows that the attractive potential energy of a pair of molecules has an inverse sixth power dependence on separation and an inverse twelfth power dependence on repulsive energy.

For polar molecules the potential function of Stockmeyer (117) is widely used for evaluating the second virial coefficient. The nature of the higher order virial coefficients are still under development.

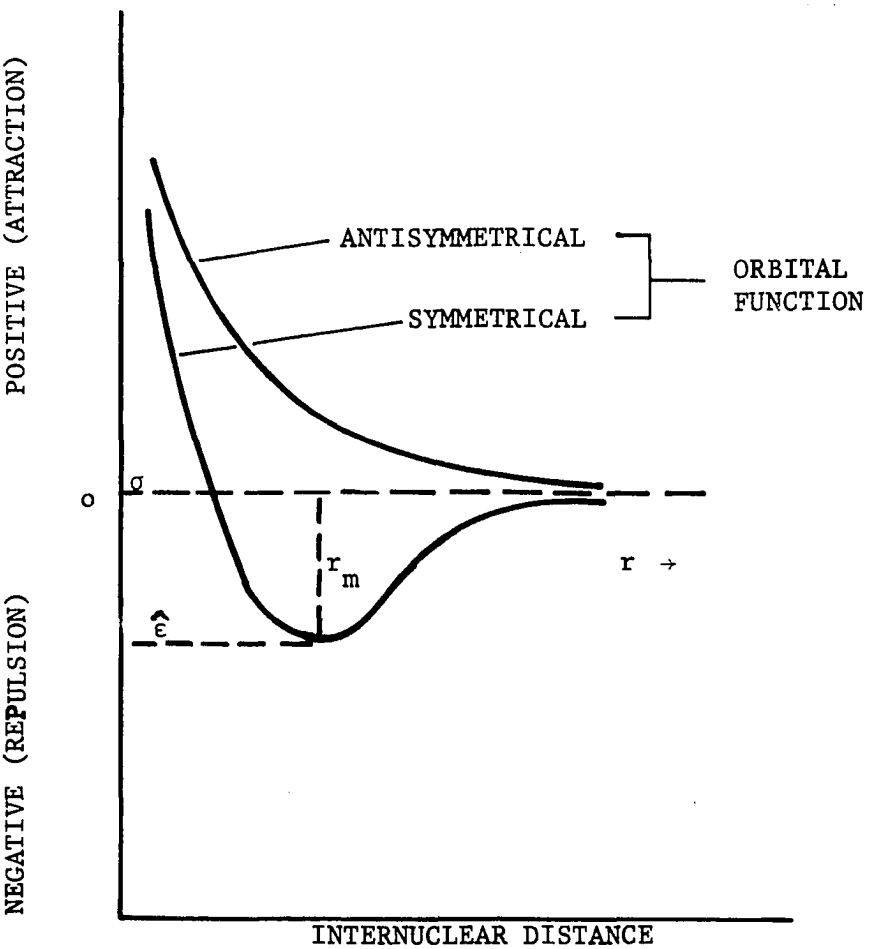


FIGURE 2-3. TYPICAL LENNARD-JONES POTENTIAL ENERGY CURVE [MOLECULAR HYDROGEN]

CHAPTER III

THIRD PARAMETERS

Over the years the approximate nature of the generalized compressibility chart, $Z = f(P_R, T_R)$, has prompted numerous investigators to improve it by introducing other parameters, or ideality correctors, in addition to P_R and T_R.

Of these numerous third parameters proposed, the two most widely accepted are Meissner and Seferian's critical compressibility factor Z_c, and Pitzer's acentric factor, ω.

In addition to the above-mentioned studies, a more recent and meritorius study by Sarem (104) proposed molecular refraction as a third parameter.

Brief summaries of these three studies follow.

A. Critical Compressibility, Z_c

Meissner and Seferian observed a linear relationship between compressibility factor at saturation pressure and the critical compressibility factor, Z_c, for 82 different compounds (see Figure 3-1). Figure (3-2) shows the relationship between factors and reduced pressures and temperatures for saturated liquids and vapors. These authors then suggested that the variation of the compressibility factors of gases at

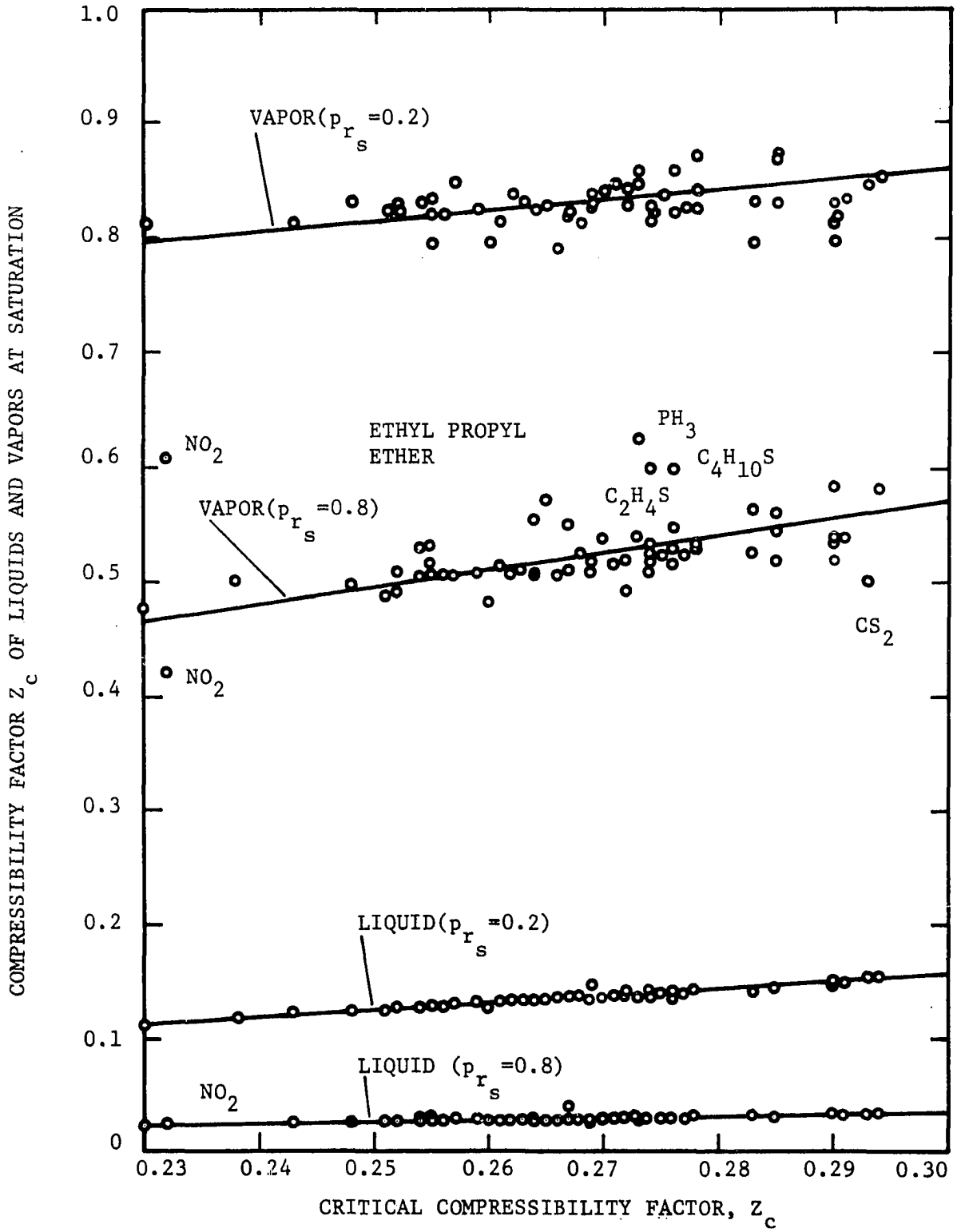


FIGURE 3-1. CORRELATION OF COMPRESSIBILITY FACTORS OF LIQUIDS AND VAPORS WITH THE CRITICAL COMPRESSIBILITY FACTOR Z_c TAKEN FROM REFERENCE 73.

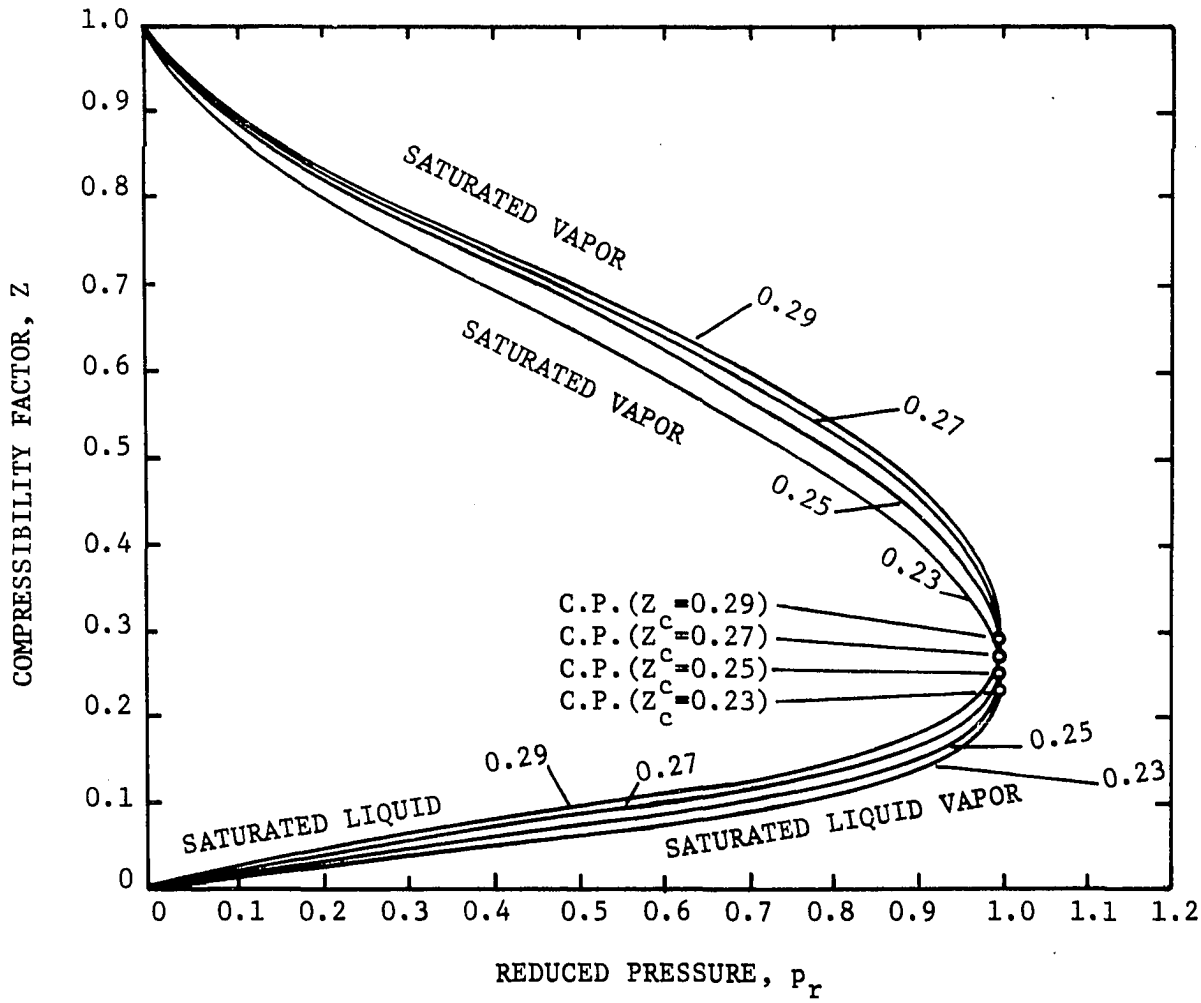


FIGURE 3-2. COMPRESSIBILITY OF SATURATED LIQUID AND VAPORS TAKEN FROM REFERENCE 73.

the critical point might be related to the variation of these compressibility factors at any other P_R and T_R.

Mathematically, the proposed equation of state can be written as

$$Z = f\ (P_R,\ T_R,\ Z_c) \tag{3-1}$$

or

$$Z/Z_{ref} = f\ \ (P_R,\ T_R,\ Z_c) \tag{3-2}$$

Kay's combination rules,

$$T_c^* = T_{c_1} X_1 + T_{c_2} X_2 + \ldots\ldots\ldots\ldots\ldots\ldots \tag{3-3}$$

$$P_c^* = P_{c_1} X_1 + P_{c_2} X_2 + \ldots\ldots\ldots\ldots\ldots\ldots \tag{3-4}$$

$$Z_c^* = Z_{c_1} X_1 + Z_{c_2} X_2 + \ldots\ldots\ldots\ldots\ldots\ldots \tag{3-5}$$

are used in conjunction with reference compressibility charts.

B. Pitzer's Acentric Factor, ω

Pitzer introduced the acentric factor as a correction for the deviation of the intermolecular potential of a substance from that of simple spherical molecules, $Z = f\ (P_R,\ T_R,\ \omega)$. The acentric factor itself is empirically chosen in terms of reduced saturation pressure at a reduced temperature of 0.70. Mathematically, the relationship can be shown thus:

$$\omega = 0 \text{ (for a simple fluid)}$$

$$\omega = -\log \frac{P_s}{P_c} - 1.0 \tag{3-6}$$

and,

$$Z = Z^{o}\ (P_R, T_R) + \omega' Z^{(1)}\ (P_R, T_R) \qquad (3\text{-}7)$$

Z^{o} and $Z^{(1)}$ are obtained from plots similar to that shown in Figure 3-3. For a given reduced temperature, Z^{o} is the intercept at ω=o and $Z^{(1)}$ is the slope of the curve.

In this method Kay's rule is also recommended for obtaining pseudo critical properties, and ω_{mix} is

$$\omega_{mix} = \omega_1 X_1 + \omega_2 X_2 + \ldots\ldots \omega_n X_n \qquad (3\text{-}8)$$

C. Lorentz-Lorenz, R_D

Sarem proposed the Lorentz-Lorenz molecular refraction, R_D, as a third parameter to characterize a given system with regards to non-ideality. Mathematically expressed $Z = f\ (P_R, T_R, R_D)$, where

$$R_D = \left[\frac{n^2-1}{n^2+2}\right] \frac{MW}{\rho} = \Pi_E = \frac{4}{3}\,\pi\, N\alpha_E \qquad (3\text{-}9)$$

where:

Π_E = electronic polarization measured by the D-line of sodium

ρ = density

α_E = electronic polarizability

n = refractive index

MW = molecular weight

N = Avogadro number

For predicting the compressibility factor of mixtures, the molar average molecular refraction is determined by the formula,

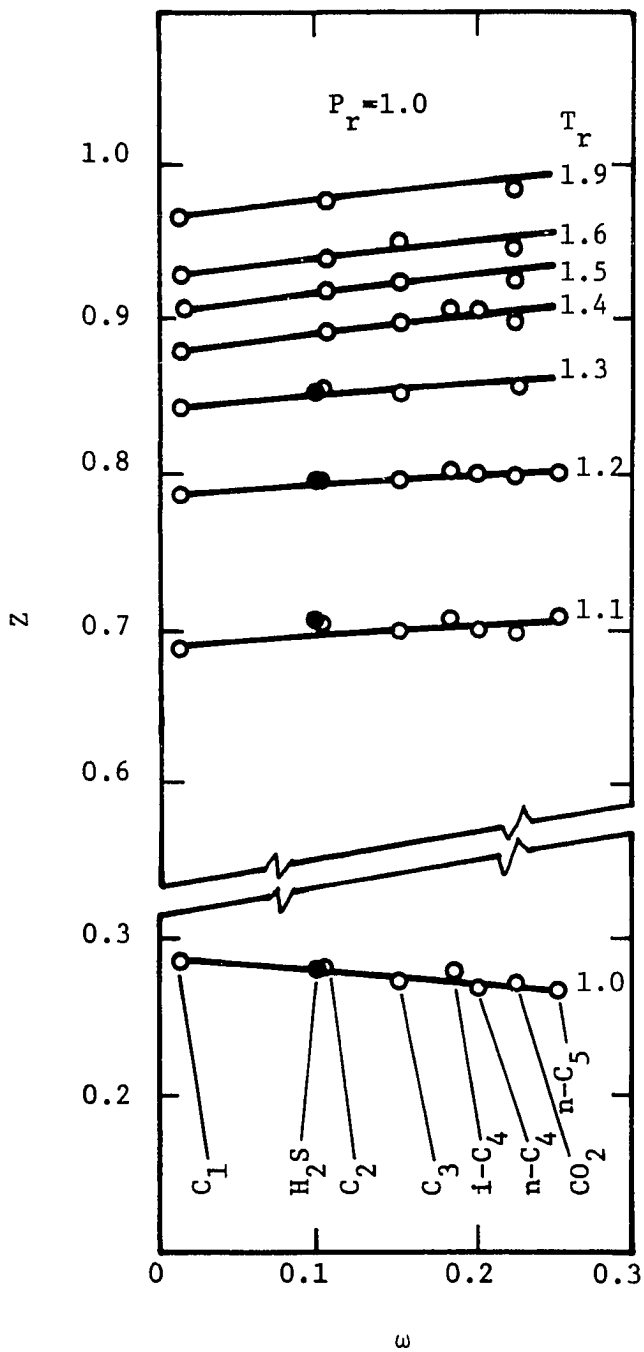


FIGURE 3-3. THE COMPRESSIBILITY FACTOR AS A FUNCTION OF ACENTRIC FACTOR AT P_r = 1.0 AND THE VALUES OF T_r INDICATED, REFERENCE 105.

$$R_{D_{mix}} = \sum_{i=1}^{\hat{n}} X_i R_{D_i} \tag{3-10}$$

and a normal pure hydrocarbon which has a molecular refraction equivalent to the value of $R_{D_{mix}}$ is chosen. (This could also be done by interpolating between two reference substances.) Then look up the compressibility factor for the reference substance at the temperature and pressure conditions.

The proposed combination rule is that of Leland and Mueller, and is as follows for vapor mixtures.

$$T_c^* = \left[\frac{\sum_{i=1}^{\hat{n}} \sum_{j=1}^{\hat{n}} x_i x_j \left(\frac{Z_c T_c^{\alpha+1}}{P_c} \right)_i^{0.5} \left(\frac{Z_c T_c^{\alpha+1}}{P_c} \right)_j^{0.5}}{\sum_{i=1}^{\hat{n}} \sum_{j=1}^{\hat{n}} x_i x_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_i^{0.333} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_j^{0.333} \right]^3} \right]^{1/\alpha} \tag{3-11}$$

$$P_c^* = \frac{T_c^* \sum_{i=1}^{\hat{n}} x_i (Z_c)_i}{\sum_{i=1}^{\hat{n}} \sum_{j=1}^{\hat{n}} x_i x_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_i^{0.333} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_j^{0.333} \right]^3} \tag{3-12}$$

where α is empirically determined to be a function of temperature and pressure as follows:

$$\alpha = -.75\left(\frac{P\sum_i X_i T_{c_i}}{T\sum_i X_i P_{c_i}}\right) + 2.44 \text{ for } 0.4 < F = \frac{P\sum_i X_i T_{c_i}}{T\sum_i X_i P_{c_i}} < 2.0. \tag{3-13}$$

$\alpha = 2.2$ for $F \leq 0.4$, $\alpha = 1.0$ for $F \geq 2.0$

For saturated liquids mixtures set $\alpha = 1.0$, the combination rule now is,

$$T_c^* = \left[\frac{\sum_{i=1}^{\hat{n}}\sum_{j=1}^{\hat{n}} X_i X_j \left(\frac{Z_c T_c}{P_c}\right)_i^{\alpha+1} \left(\frac{Z_c T_c}{P_c}\right)_j^{0.5}}{\sum_{i=1}^{\hat{n}}\sum_{j=1}^{\hat{n}} X_i X_j \left(\frac{Z_c T_c}{P_c}\right)_i^{0.5} \left(\frac{Z_c T_c}{P_c}\right)_j^{0.5}}\right]^{1/\alpha} \tag{3-14}$$

and,

$$P_c^* = \frac{T_c^* \sum_{j=1}^{\hat{n}} X_j (Z_c)_j}{\sum_{i=1}^{\hat{n}}\sum_{j=1}^{\hat{n}} X_i X_j \left(\frac{Z_c T_c}{P_c}\right)_i^{0.5} \left(\frac{Z_c T_c}{P_c}\right)_j^{0.5}} \tag{3-15}$$

D. Critique of R_D

Sarem adequately showed the suitability of molecular refraction as a third parameter. However, both the choice of molecular refraction formula and the proposed method of use of this parameter deserves comment.

Lorentz-Lorenz, in arriving at the constancy of their molecular refraction formula, calculated the electronic polarization on an

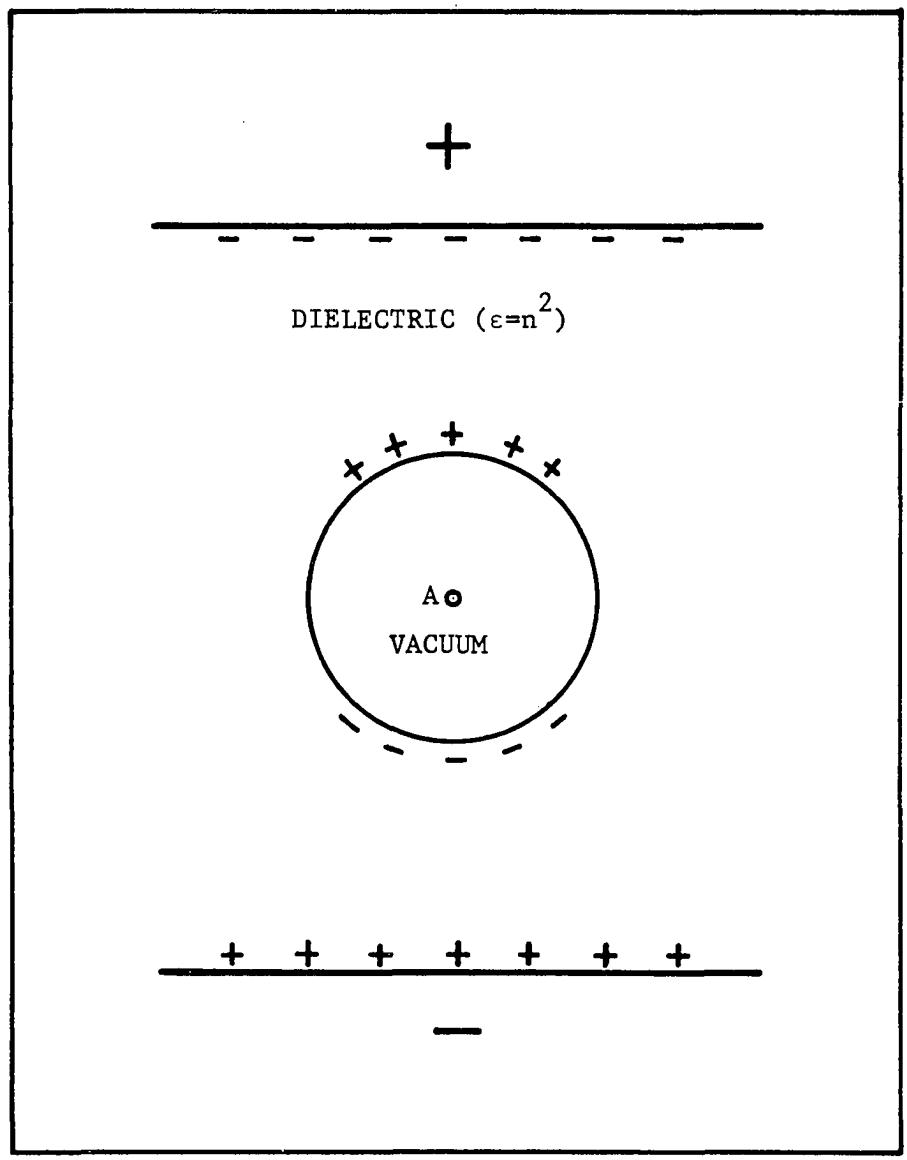


FIGURE 3-4. PICTORIAL REPRESENTATION OF LORENTZ-LORENZ SPHERICAL CAVITY CONCEPT, REFERENCE 64.

electron by assuming that the electron was at the center of a spherical cavity (see Figure 3-4), the polarization on the walls of which produced the field at the center.

This optical isotropic concept assumes that the molecules are sufficiently widely separated so that they do not affect each other's orientation. It is obvious that this condition is more likely satisfied in the vapor phase and not in the liquid. Moreover, it is generally agreed by experts on light scattering that all known molecules are anisotropic, that is, polarizable to different extents in different directions. This means that the refractivity of a liquid is in reality an average effect brought about by the individual contribution of the various molecules oriented relative to one another and to the field of incident radiation. Hence the reason why the Lorentz-Lorenz equation is different in the gaseous phase to the liquid phase.

Acceptance of Sarem's approach whereby one chooses a reference substance is hindered by the fact that:

1. The Lorentz-Lorenz molecular refraction formula (R_D) is neither constant when going from the gaseous to the liquid state nor at elevated temperatures and pressures.
2. The additivity of R_D is only true for a given homogeneous series. Sarem's method contains no recommendation for fluid systems containing polar compounds or other non-paraffinitic hydrocarbons. Since different series or combination of series can have the same R_D, it is not hard to visualize the predicament one can get into in trying to choose the correct reference substance.

CHAPTER IV

MOLECULAR REFRACTION

To be able to predict physical properties from known constitution and structure is undoubtedly of tremendous value both from a theoretical as well as practical point of view. These physical properties are vital in predicting pressure, volume, and temperature behavior.

We know from wave mechanics that it is theoretically possible to determine the electronic structure of molecules by solving the Schrodinger wave equations. However, in actual practice, an exact solution of the Schrodinger equation is only possible in the simplest and most idealized cases, such as one electron present in one atom, or one atom in one molecule. However, by measuring the refractive index of a substance, it is possible to obtain a great deal of information concerning the electronic structure of the constituting atoms and molecules.

The electric field, set up by an incident light wave, induces a forced vibration among the molecules. This reaction of the molecules is responsible for the refractive index.

The molar volume of a substance is the ratio of the molecular weight to the density and is an additive and constitutive property. Molar or molecular refraction is the product of a dimensionless function of refractive index multiplied by the molar volumes of the substance

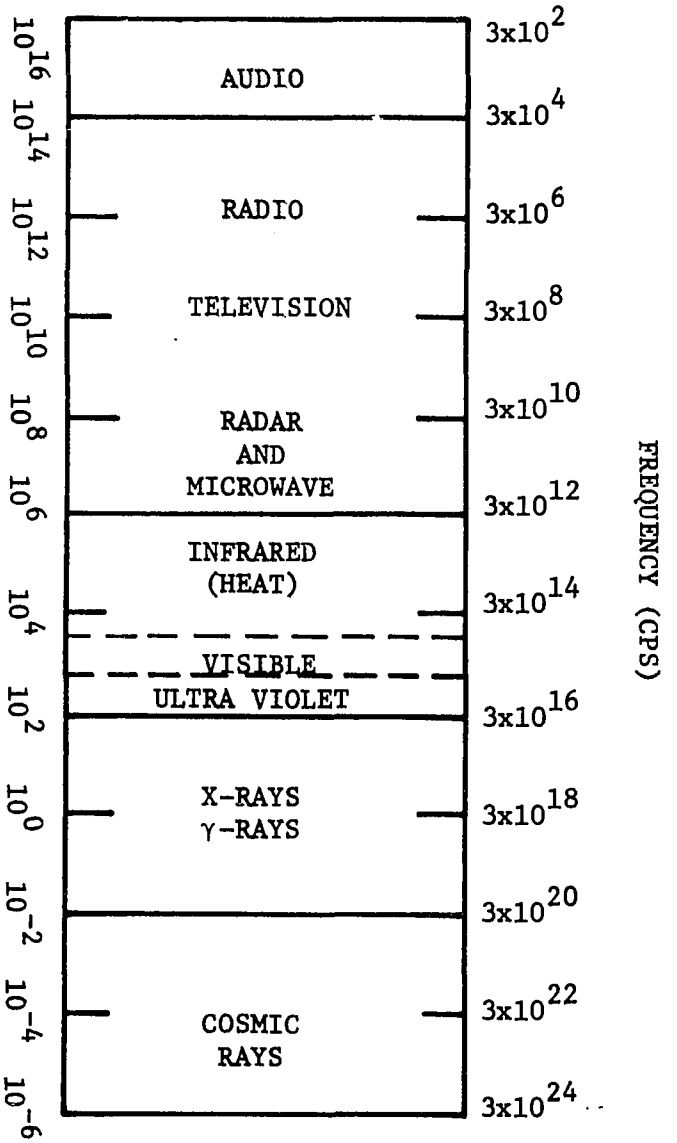


FIGURE 4-1. THE ELECTROMAGNETIC SPECTRUM

under consideration. Molecular refraction is a characteristic property of any substance in the gaseous, liquid, or solid state, from which details on structure could be obtained.

Today the two most widely accepted equations for computing molecular refractions are the Lorentz-Lorenz equations and the Eykman equation. The former is highly theoretical and is based on Maxwell's electromagnetic theory of light, while the latter is empirically reliable in both simple and complex systems.

A. Lorentz-Lorenz Equation

Based on Maxwell's classical theory of dielectrics and the assumption that all molecules of a substance are spherical perfect conductors, Classius was able to show the following relationship:

$$\varepsilon = (1+2\xi)/(1-\xi) \tag{4-1}$$

where ε = Maxwell's dielectric constant

$$\xi = \frac{\text{volume occupied by the molecules}}{\text{volume apparently occupied by the molecules}}$$

Upon expanding we have:

$$\varepsilon - \varepsilon\xi = 1+2\xi \tag{4-2}$$

$$-\varepsilon\xi-2\xi = 1-\varepsilon \tag{4-3}$$

$$\xi(\varepsilon+2) = \varepsilon-1 \tag{4-4}$$

$$\xi = \frac{\varepsilon-1}{\varepsilon+2} \tag{4-5}$$

Maxwell has shown that for a non-magnetic media, the dielectric constant was equal to the square of the refractive index provided that the same wave length of electronic vibration was used. The common practice is to measure the refractive index (hence, molecular refraction) in the region

of visible light utilizing the yellow light (about 5893 Å) of the Sodium D line (see Figure 4-1).

So we may write

$$\xi = \frac{(n^2-1)}{(n^2+2)} \qquad (4\text{-}6)$$

It is now possible to conclude that the dimensionless refractive index function ξ is the true volume of the molecules in unit volume. If ρ is the density of the substance, then ρ/ξ is the true density of the molecules, without intermolecular spaces, while the reciprocal ξ/ρ would be the true volume of unit mass of the molecules. If W is designated as the absolute weight of a molecule of the substance, then the true volume of a molecule should be $\xi W/\rho$. However, if instead of W we substitute MW, molecular weight, then we have the ever famous Lorentz-Lorenz molecular refraction equation:

$$R_D = \xi MW/\rho = [(n^2-1)/(n^2+2)]\,\frac{MW}{\rho} \qquad (3\text{-}9)$$

Because molecular refraction has the dimensions of volume many authors have referred to it as the true molar volume. However, this is not absolutely correct for the mere reason that molecular weights are relative numbers; molecular weights as they are generally used is not the absolute weight of the actual molecules in a volume of substance. It is for this reason that R_D in the above equation is in actual fact, proportional to the true volume of the molecule in a gram molecular quantity of the substance.

B. Eykman Equation

As already mentioned, this equation is purely empirical. In 1895

Eykman, while examining the constancy of the Gladstone and Dale, and the Lorentz-Lorenz specific refraction formula for different homologous series at elevated temperatures found that:

1. The Gladstone and Dale formula $(n-1)/\rho$ gave low values.
2. The Lorentz-Lorenz formula $[(n^2-1)/(n+2)]\ \frac{1}{\rho}$ gave high values.

Eykman then proceeded to compare the two molecular refraction formulas.

$$(n-1)MW/\rho \qquad \text{Gladstone and Dale} \qquad (4\text{-}8)$$

$$[(n^2-1)/(n^2+2)]\ MW/\rho \qquad \text{Lorentz-Lorenz} \qquad (4\text{-}9)$$

He observed that the only difference between the two formulas was the denominator inasmuch as the Gladstone and Dale formula can also be written as

$$[(n^2-1)/(n+1)]\ \frac{MW}{\rho}. \qquad (4\text{-}10)$$

He reasoned that since the two curves were in fact continuous functions, somewhere between these functions must lie another continuous function of refractive index such that $(n^2-1)/\phi(n)$ varies with changes in temperature in the same proportion to density. The formula satisfying the curve of the desired function is

$$[(n^2-1)/(n+0.4)]\ \frac{MW}{\rho} \qquad (4\text{-}11)$$

In his research he showed that at 120°C, the deviations for the Lorentz-Lorenz formula were of the order of +0.7 to 1.3 per cent, whereas the proposed formula was of the order of $\pm$ 0.1 per cent.

C. EMR and Optical Properties at the Critical Point

Theoretically the view is held that the velocity of light is the same through all substances at the critical point, and as such all substances should have the same refractive index at the critical point. Using numerous diverse organic compounds, Smith (109) showed the critical refractive index to be nearly equal to the theoretical value of 1.126. By solving the Eykman equation in the following form,

$$n_c - \frac{0.84}{n_c + 0.4} = \frac{\rho_c}{MW}\left[2.185 + 0.7357\ MW\right], \qquad (4\text{-}12)$$

a value of approximately 1.127 is obtained for the critical refractive index of "normal" oil field fluid components. Table 4-1 shows the critical refractive indices for several components of interest.

There exist equally valid correlations between Eykman Molecular Refraction and other critical properties. Figures 4-2, 4-3, and 4-4 show a regular relationship between critical density, temperature and pressure, viscosity, and critical compressibility of the normal hydrocarbons with Eykman Molecular Refraction.

Previous investigators have proposed equations for determining critical temperatures, pressures and volumes making use of molecular refraction. Wan (127) suggested

$$T_c = 7.02\ R_D + 23.1 \text{ (for liquid paraffin hydrocarbons)} \qquad (4\text{-}13)$$

Meissner (76) proposed the following relationship:

$$T_c = [5850\ [R_D]^2 + C]/(P_a)^{1.65} \qquad (4\text{-}14)$$

$$V_c = 0.55\ [1.5\ (P_a) + 9 - 4.34\ (R_D)\ ]^{1.155} \qquad (4\text{-}15)$$

$$P_c = 60.3\ T_c/[1.5\ (P_a) + 9 - 4.34\ (R_D)\ ]^{1.226} \qquad (4\text{-}16)$$

where: T_c = critical temperature, °C

P_c = critical pressure, atmospheres

V_c = critical volume, cubic centimeters per gram mole

P_a = Sugden's parachor

$$= \frac{(MW)\ \overline{\gamma}^{\ 1/4}}{\rho}$$

MW = molecular weight

$\overline{\gamma}$ = surface tension in dynes per centimeter

ρ_g = the vapor density in grams per cubic centimeter

ρ_L = liquid density in grams per cubic centimeter

C = a constant depending on the class of compound

D. Summary

There is one and only one way that any molecular refraction equation, highly theoretical or purely empirical must prove itself, and that is by its ability to predict successfully the dependence of refractive index on temperature and pressure. The Eykman form of the molecular refraction equation has been shown in recent years to represent well the effect of pressure and temperature on the relationship between density and refractive index.

Considerable evidence exists that shows that the Lorentz-Lorenz molecular refraction specifies too large a change in refractive index for a given increment of density when refractive index and density change as a result of changing temperature and

pressure. This means that R_D is more precisely represented mathematically as

$$R_D = \left[\frac{n^2-1}{n^2+2}\right]\frac{MW}{\rho} = \Pi_E = \frac{4\pi}{3} + \gamma)\ N\alpha_E \qquad (4\text{-}17)$$

where: $\gamma = f(\rho)$.

Figure 4-5 is a comparison of the Lorentz-Lorenz and Eykman specific refractive index functions for the isothermal compression of pentane. The curves all show less deviation with the Eykman equation. Figure 4-6 shows the inability of the Lorentz-Lorenz refractive intercept to predict correctly the dependence of refractive index on pressure. The dotted line represents the predicted curve, and the circles the experimental values. Figures 4-7 and 4-8 are other comparisons of experimental pressure-temperature-refractive index relationships using the Lorentz-Lorenz molecular refraction relationship and that of Eykman.

TABLE 4-1

CRITICAL REFRACTIVE INDICIES

Component	Smith Ref. (109)	Equation 4-12 and Density from API Project 44	Extrapolated Value From Ref. (1)
Gases and Vapors			
Oxygen	1.126	-	-
Carbon Dioxide	1.124	-	-
Sulphur Dioxide	1.128	-	-
Methane	-	-	1.126
Inorganic Liquids and Condensed Gases			
Oxygen	1.124	-	-
Carbon Dioxide	1.101	-	-
Sulphur Dioxide	1.126	-	-
Hydrogen Sulphide	1.146	-	-
Organic Liquids			
n-Pentane	1.125	-	-
n-Heptane	-	1.128	-
n-Octane	-	1.127	-
n-Nonane	-	1.127	-
n-Decane	-	1.127	-
n-Undecane	-	1.127	-
n-Dodecane	-	1.127	-

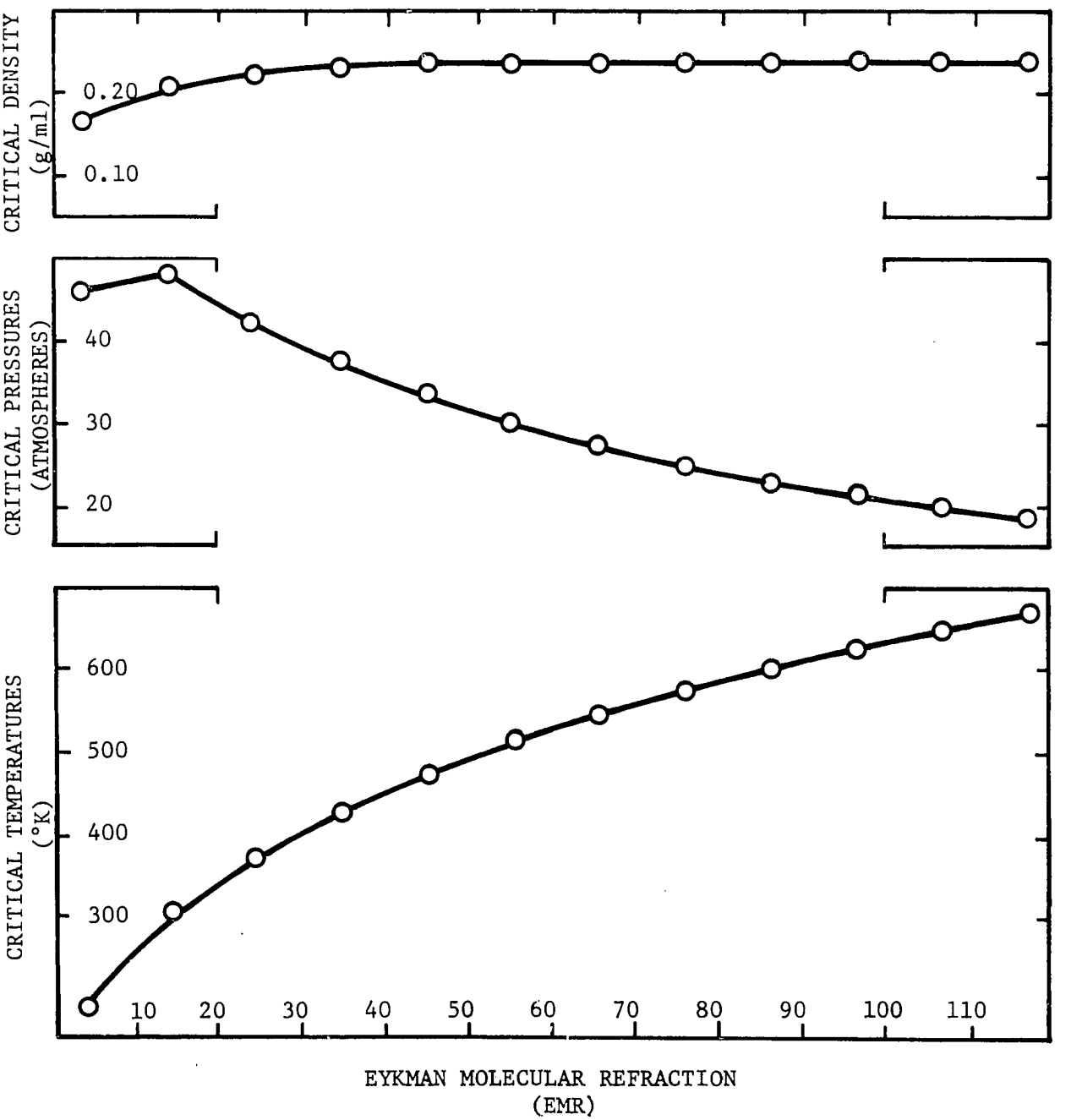


FIGURE 4-2. CORRELATION OF CRITICAL PROPERTIES OF NORMAL HYDROCARBONS AND EMR.

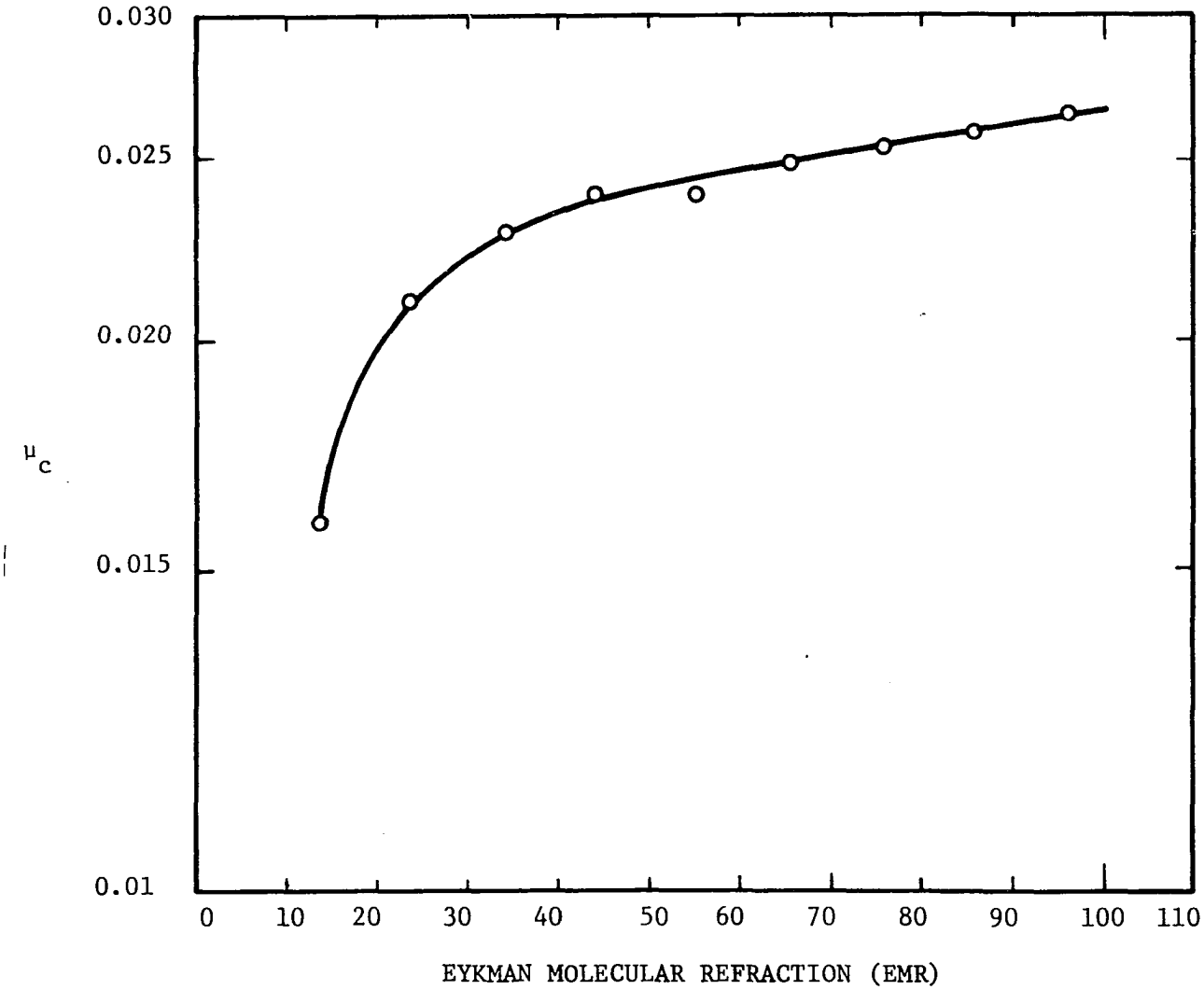


FIGURE 4-3. CORRELATION OF CRITICAL VISCOSITY OF NORMAL HYDROCARBONS AND EMR

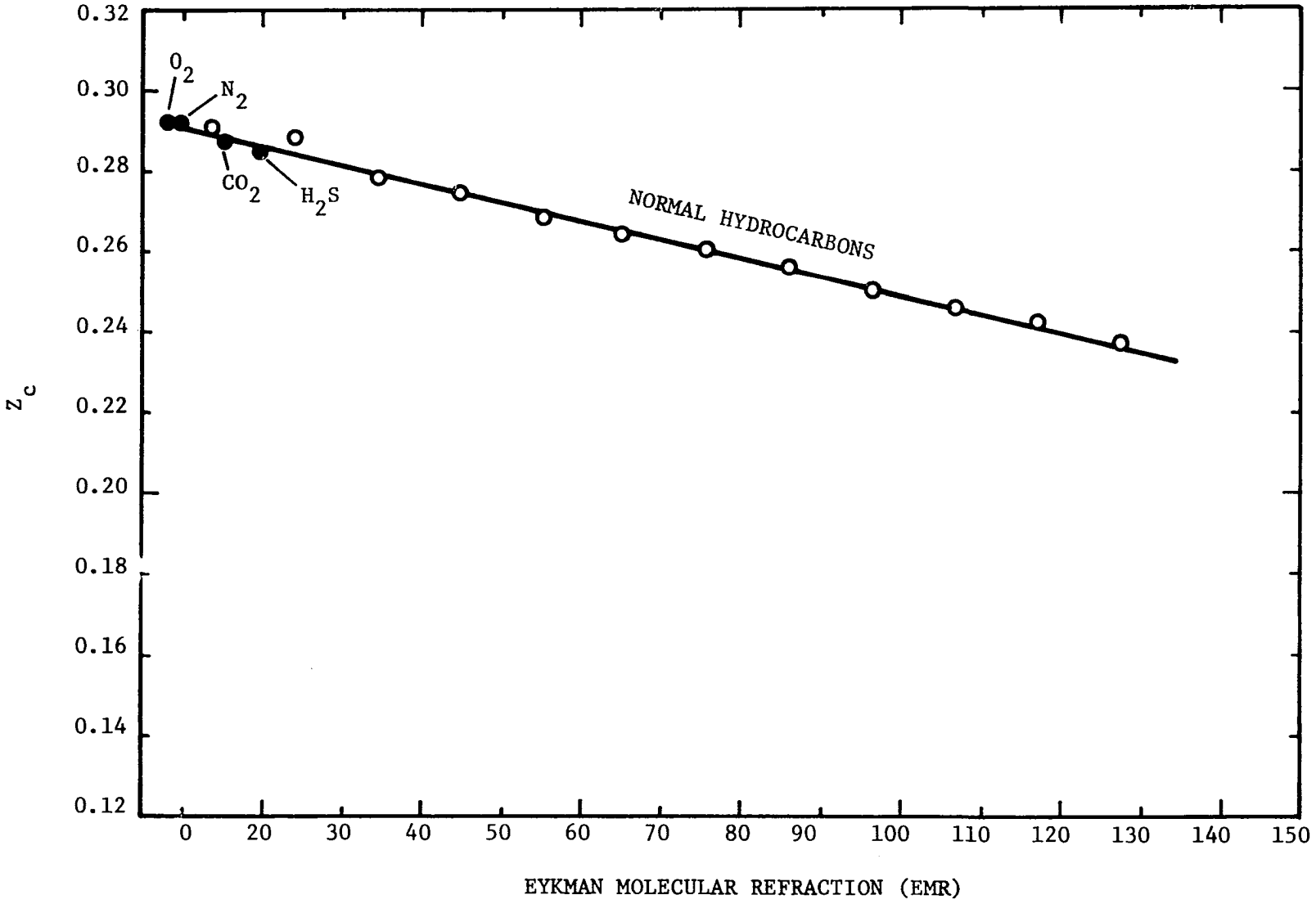


FIGURE 4-4. CORRELATION OF CRITICAL COMPRESSIBILITY AND EMR

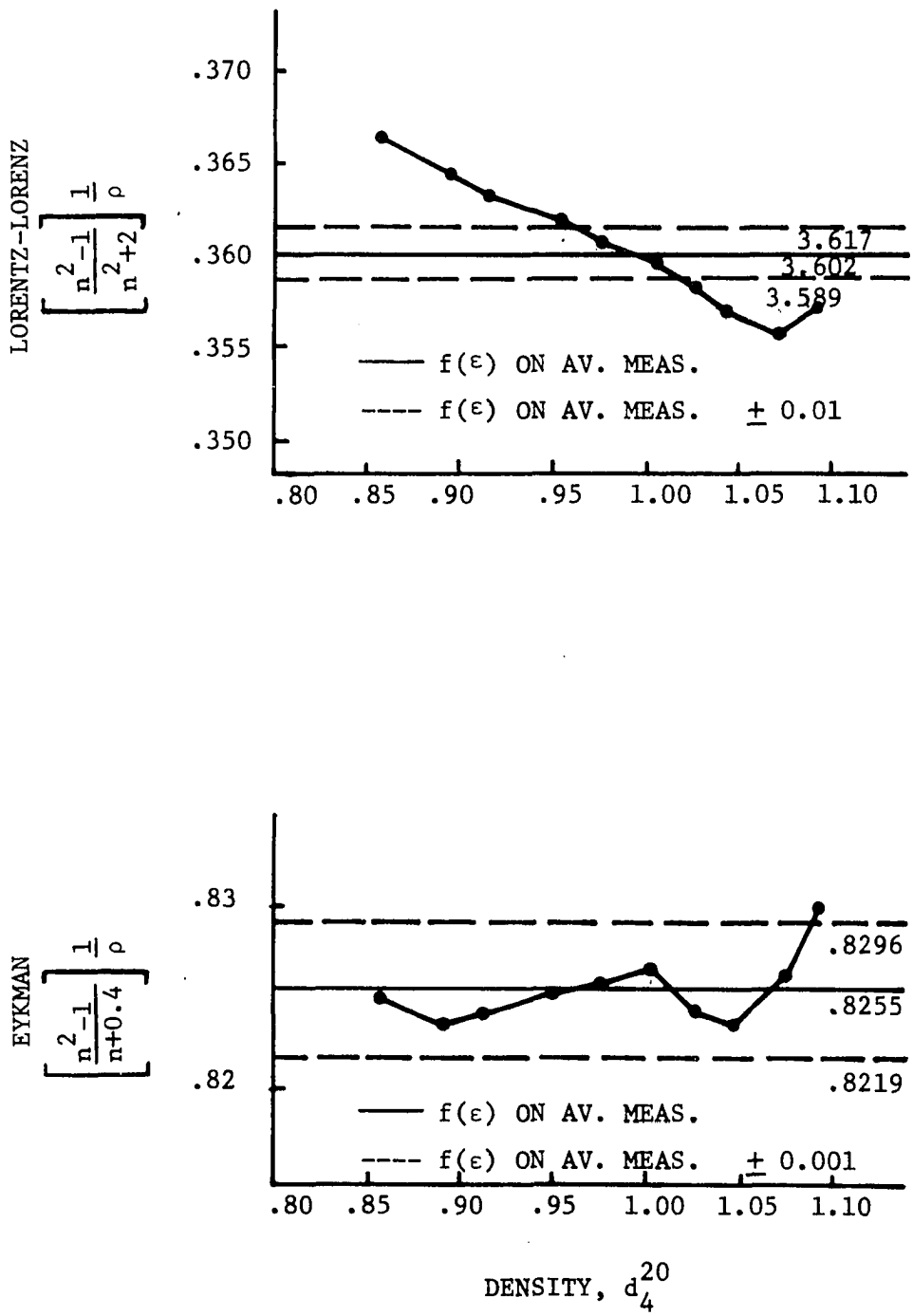


FIGURE 4-5. COMPARISON OF THE LORENTZ-LORENZ AND EYKMAN FUNCTIONS FOR THE ISOTHERMAL COMPRESSION OF PENTANE, FROM REFERENCE 22.

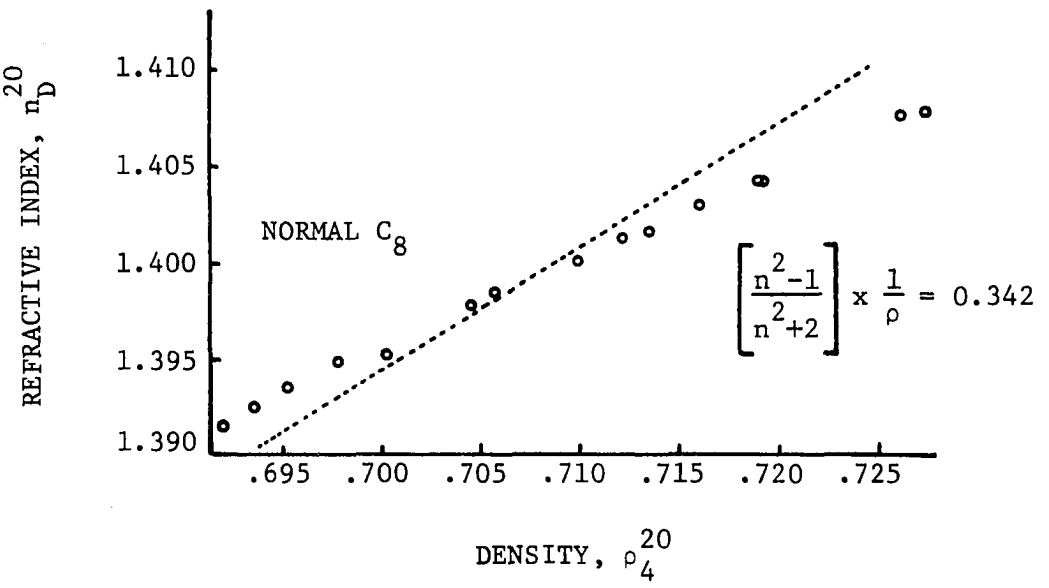


FIGURE 4-6. REFRACTIVE INDEX-DENSITY RELATION FOR C_8 PARAFFINS, REFERENCE 96.

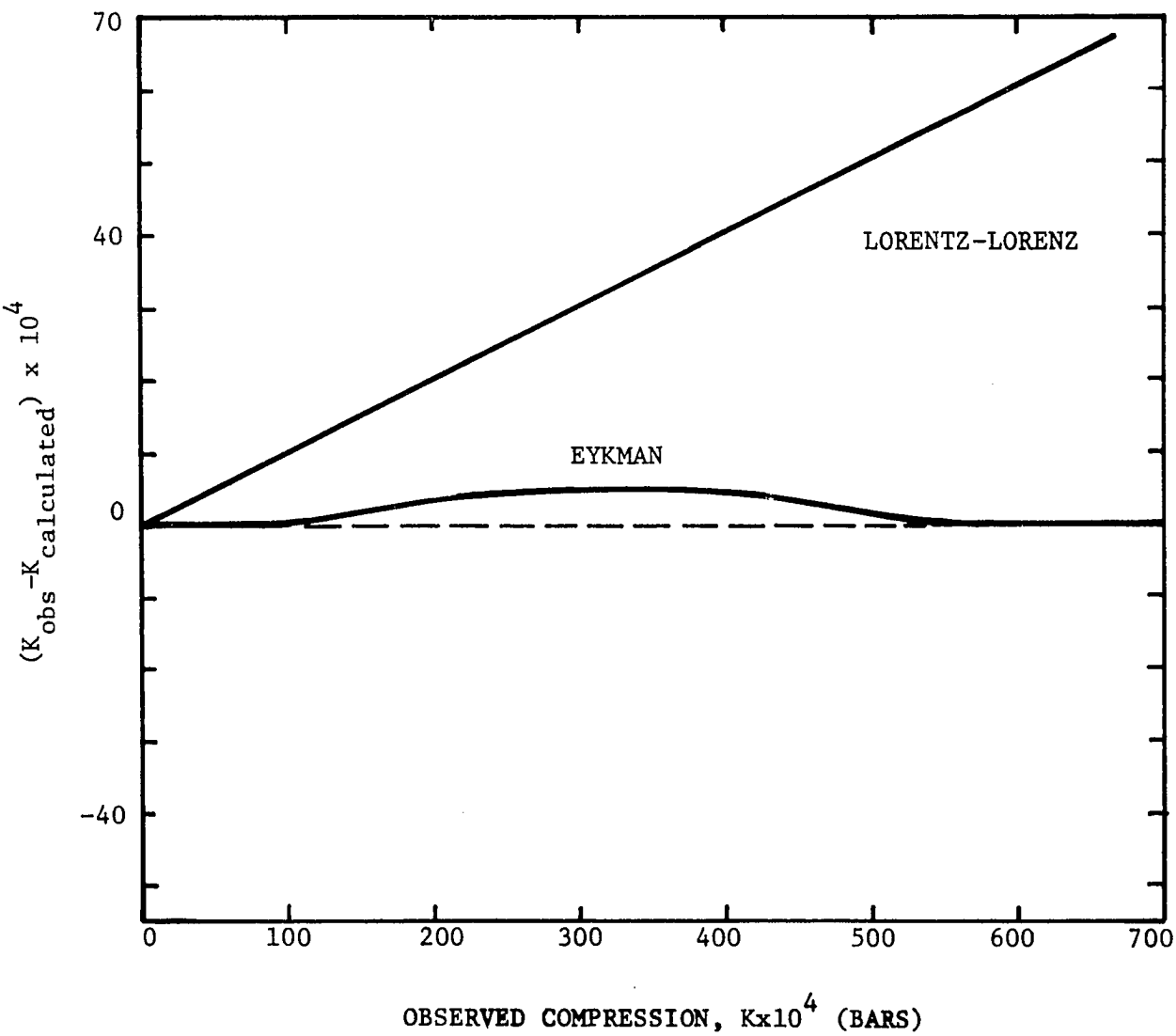


FIGURE 4-7. DIFFERENCE BETWEEN THE OBSERVED COMPRESSIONS OF BENZENE AND THOSE COMPUTED FROM THE REFRACTIVE INDICES AT THE SAME PRESSURE, FROM REFERENCE 35.

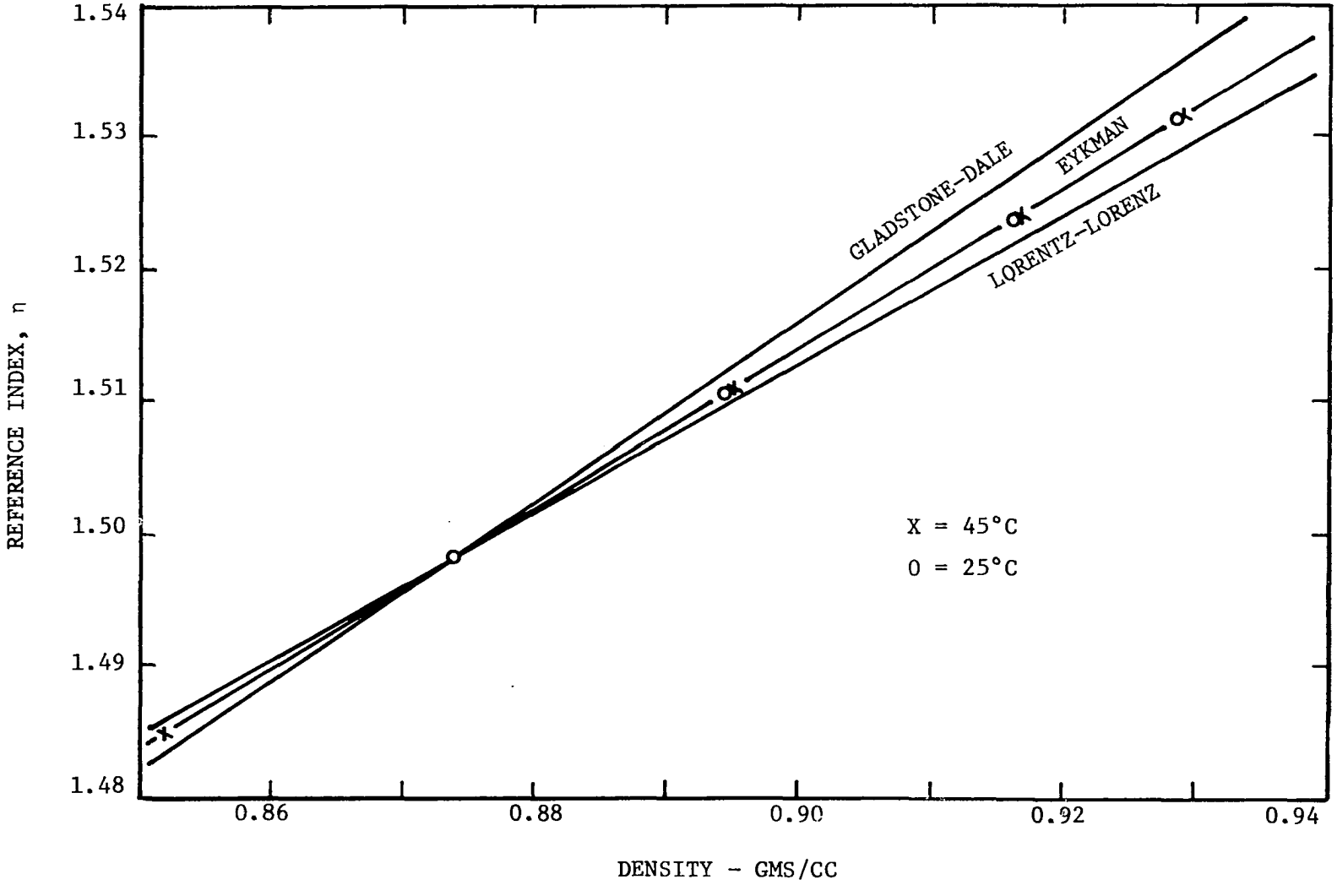


FIGURE 4-8. COMPARISON OF THE EYKMAN EQUATION WITH THE GLADSTONE-DALE AND LORENTZ-LORENZ EQUATIONS FOR BENZENE, REFERENCE 35.

CHAPTER V

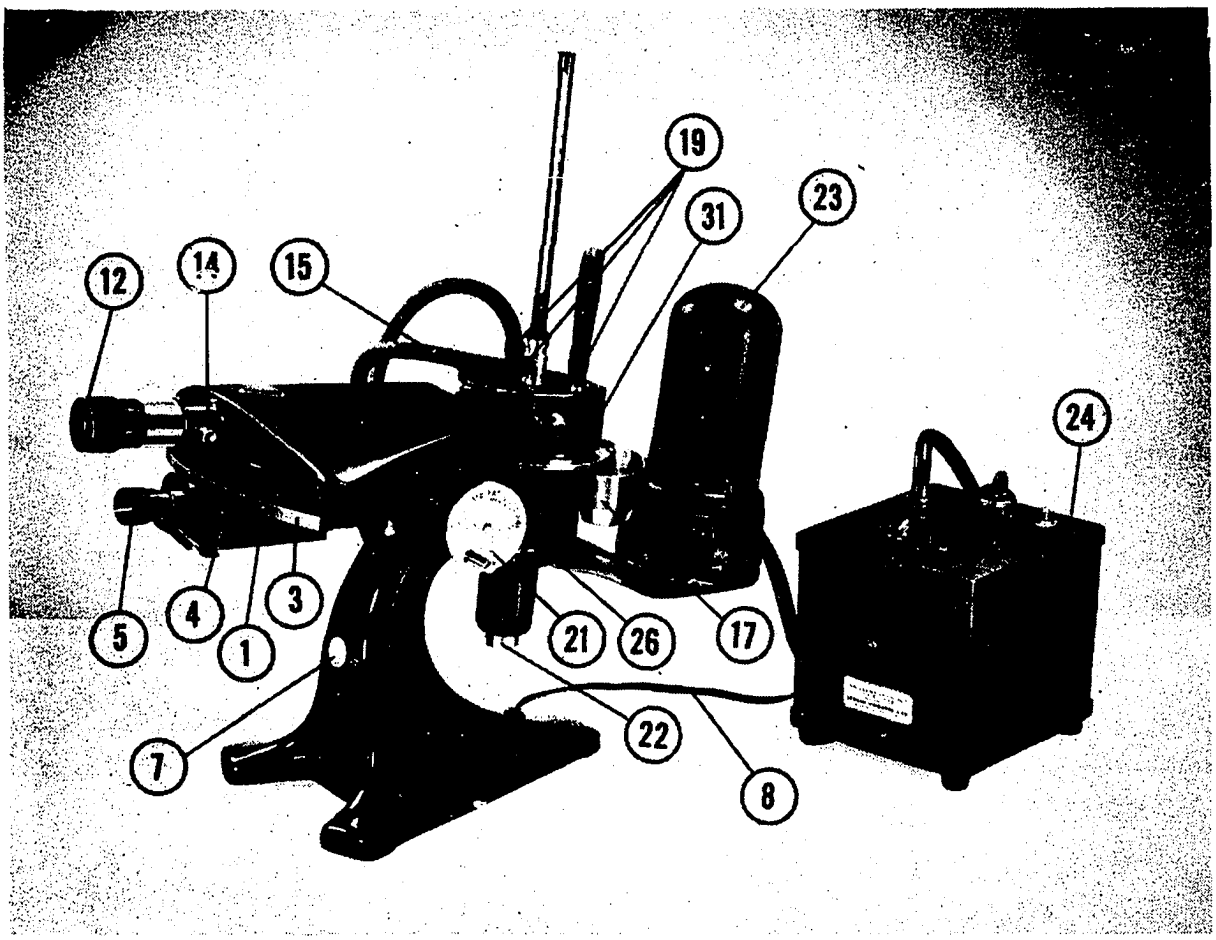
EXPERIMENTAL INVESTIGATION

Inasmuch as there exist a plentiful supply of reliable basic PVT data in the literature, there was no need for elaborate experimental work in this study. The sole purpose of the limited experiments carried out was to assist in confirming some of the characteristics of molecular refraction and for comparing the Eykman equation with the Lorentz-Lorenz equation.

A. Fluids Used

Research grade samples (99 mole per cent purity) of normal heptane, octane, nonane, decane, undecane and dodecane were used to make thirteen different mixtures. The range of the properties of which are given below:

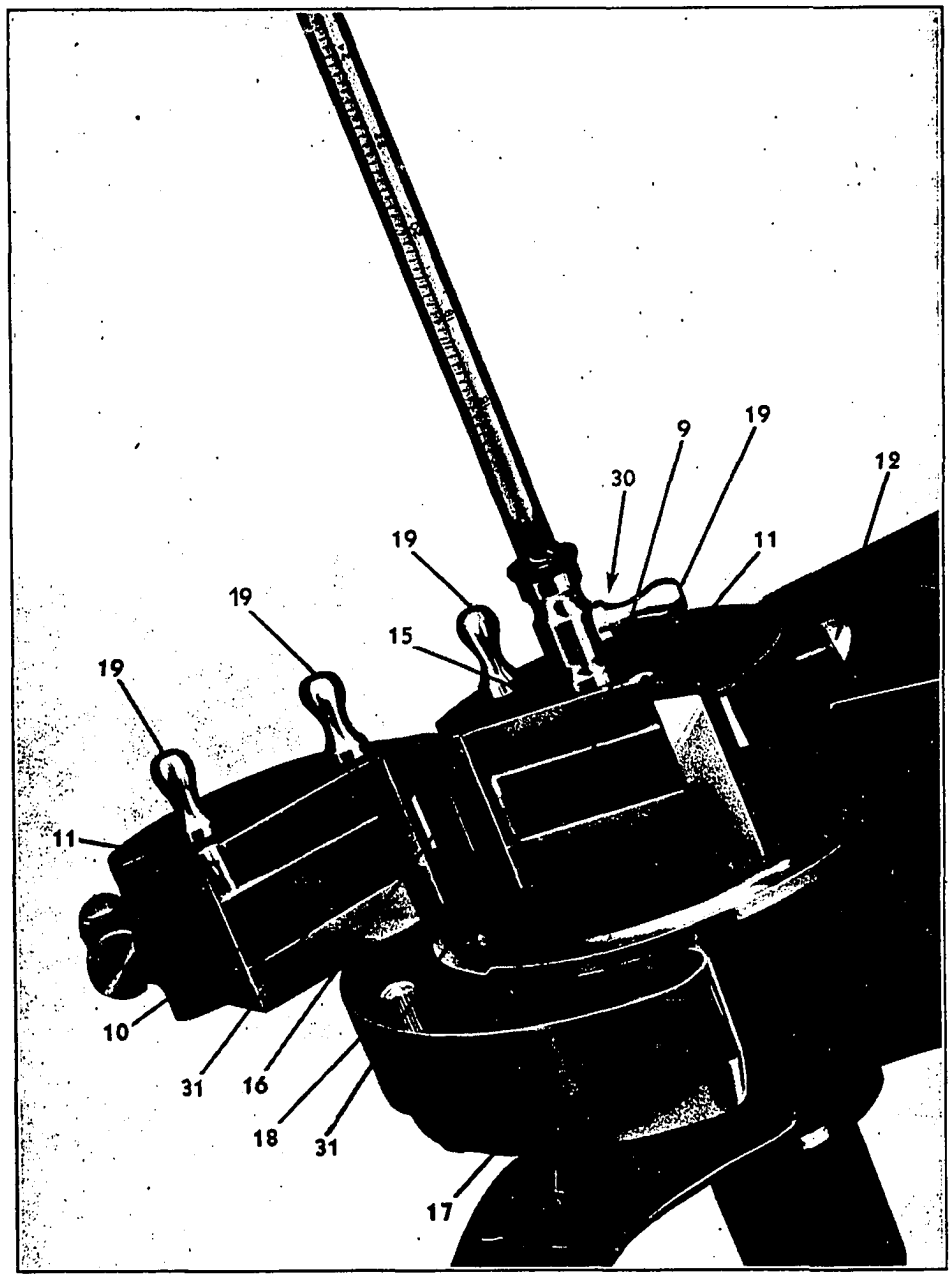
	Range
Molecular Weight	(110.6-157.7)
Density ~ gm/cc	0.6930-0.7363
Refractive Index @ 25°C	1.39271-1.41551
Eykman Molecular Refraction	83.63-118.42
μ ~ cp.	0.5080-1.123



1. ALIDADE
3. SCALE
4. VERNIER
5. SCALE MAGNIFIER
7. SCALE SWITCH
8. SCALE LAMP CONNECTOR
12. TELESCOPE
14. KNURLED HEADS
15. PRISM BOX
17. DRIP TROUGH
19. WATER CONNECTIONS
21. HAND WHEEL
22. ADJUSTING NUT
23. SODIUM LAB-ARC
24. LAB-ARC TRANSFORMER
26. LAMP BRACKET LOCK SCREW
31. PRISM HINGE

SKETCH 1

THE PRECISION REFRACTOMETER



9 - WORKING PRISM
10 - ILLUMINATING PRISM
11 - TUBULATION
12 - TELESCOPE
15 - PRISM BOX
19 - SHUTTER
17 - DRIP TROUGH
18 - DRAIN PLUG
19 - WATER CONNECTIONS
31 - PRISM HINGE

SKETCH 2

PRISM SYSTEM

B. Experimental Equipment and Procedure

A Bausch and Lomb Precision Refractometer (Figure 5-1) equipped with a sodium D lamp (5893D) was used to measure the refractive indices of both the pure components and the mixtures at 25°C.

A Precision Temperature controller (Figure 5-2) connected to the prism coupling in which the thermometer was mounted, maintained a constant temperature of 25°C $\pm$ 0.05°C on face of the prism.

The densities of the pure components and mixtures were measured two ways using (1) a Seederer-Kohlbusch chainomatic balance and (2) 10 milliter pycnometers.

Ostwald viscometers were utilized in the viscosity determinations.

CHAPTER VI

EXPERIMENTAL RESULTS

A. EMR-Molecular Weight Relationship

It has been found from this investigation that the Eykman Molecular Refraction is an additive quantity and bears a linear relationship with molecular weight (see Figures 6-1 and 6-2) for both the pure paraffin hydrocarbons and their mixtures.

$$[EMR]_{mix} = \sum_{i=1}^{\hat{n}} X_i (EMR)_i \qquad (6\text{-}1)$$

or

$$EMR_{i,i+1} = \left[\frac{n^2-1}{n+0.4}\right] \frac{M_i X_i + M_{i+1} X_{i+1}}{\rho_{i,i+1}} \qquad (6\text{-}2)$$

A similar plot to the Lorentz-Lorenz equation yields two distinct slopes - one for the light hydrocarbons and another for the heavier ones. Although the change in slope is small, it nevertheless exists.

The straight line equation for the EMR-molecular relationship is:

$$EMR = 2.185 + 0.7357\ MW. \qquad (6\text{-}4)$$

where MW = molecular weight of the paraffin pure component or mixture.

Table 6-1 is an error analysis of the curve fit. It shows an average error of 0.0 per cent and an average absolute error of 0.055 per cent.

Based on all comparative studies in this investigation, the Eykman equation was found to be superior to that of Lorentz-Lorenz and was therefore used for all final correlations.

B. EMR-EMRI-Density Relationship

A useful function (within a homologous series) in the analysis of complex liquid hydrocarbon mixtures is the Eykman Molecular Refractivity Intercept (EMRI).

$$EMRI = ((n^2-1)/(n + 0.4))/\rho \qquad (6\text{-}5)$$

The superiority of fit seen in Figure 6-3 (along with the verification in the literature) means that there exists an easily measurable characterization parameter for any complex hydrocarbon systems containing heptane plus. All that is necessary is to measure the density of the heptanes plus at any temperature and then go to the plot of EMR versus density squared, at various temperatures (Figure 6-4). The molecular weight of the heptanes plus is easily obtained by substituting the value of EMR into the following equation:

$$\text{Mol. Wt.} = -2.970 + 1.3591\ EMR \qquad (6\text{-}6)$$

An equally valid approach is to measure the density of the heptanes plus at any temperature, then enter the plot of EMRI versus density (Figure 6-3), with the value of EMRI enter a plot of EMRI versus EMR (Figure 6-5) or MW (Figure 6-6), depending upon the parameter of interest.

The ease and preciseness of this technique is particularly significant. Neither is possible to this degree when using other third parameters with mixtures showing the heptanes plus as the heaviest fraction.

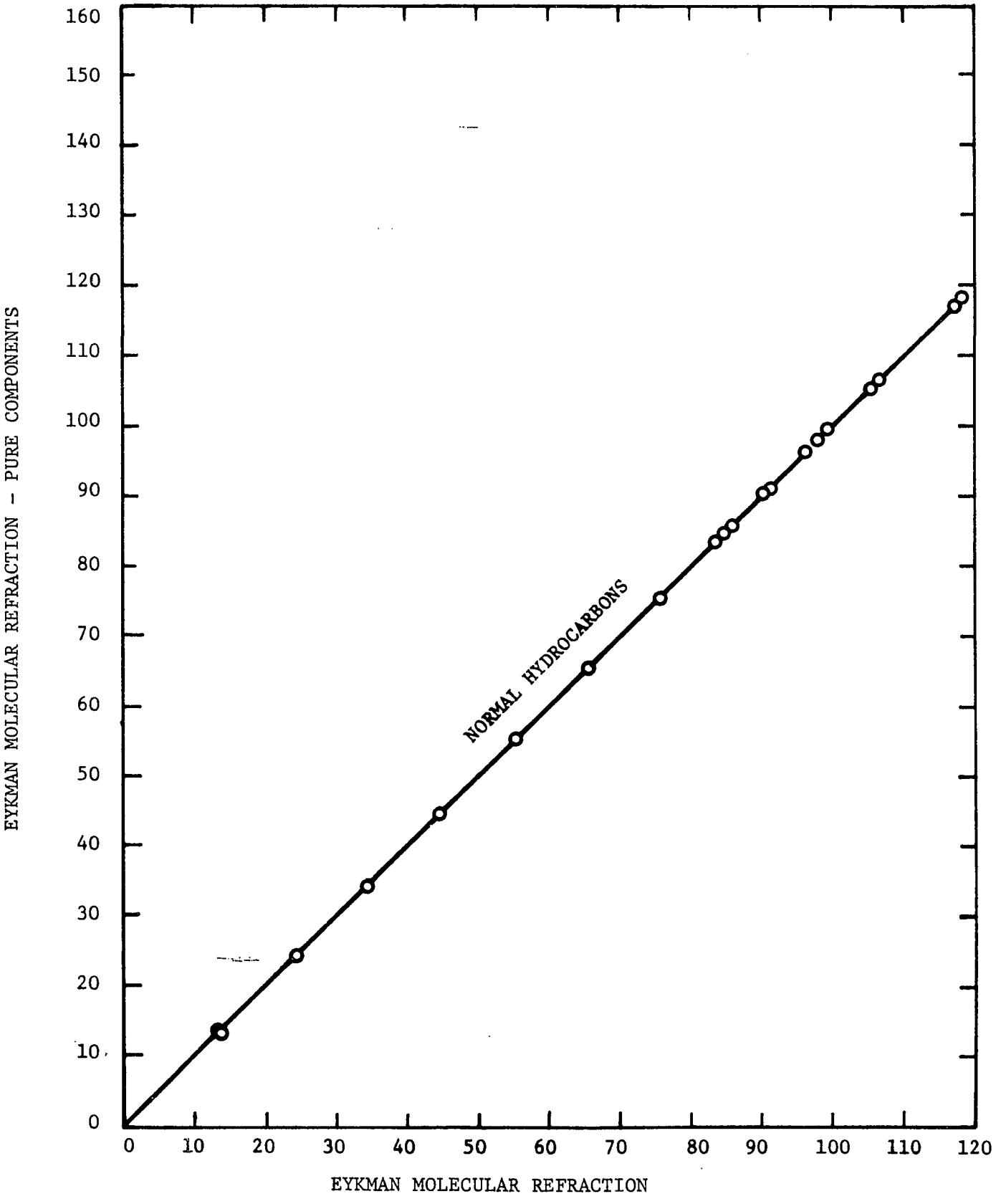


FIGURE 6-1. CORRELATION OF EMR PURE COMPONENTS AND EMR PROPOSED EQUATION (6-4).

TABLE 6-1

CURVE FIT AND ERROR ANALYSIS OF MOLECULAR WEIGHT

WITH EYKMAN MOLECULAR REFRACTION

Eykman Molecular Refraction	Molecular Weight	Calculated Molecular Weight	Per Cent Deviation
16.042	13.987	13.988	-0.010
30.068	24.307	24.307	-0.003
44.094	34.628	34.627	0.001
58.120	44.948	44.946	0.002
72.146	55.302	55.266	0.064
86.172	65.575	65.585	-0.016
100.198	75.875	75.905	-0.039
110.578	83.630	83.542	0.105
112.495	85.046	84.952	0.109
114.224	86.193	86.224	-0.036
120.042	90.463	90.505	-0.046
120.346	90.584	90.728	-0.159
121.346	91.458	91.464	-0.007
127.906	96.351	96.291	0.062
128.250	96.529	96.544	-0.015
130.449	98.228	98.162	0.067
132.462	99.730	99.643	0.087
133.145	99.991	100.145	-0.154
140.468	105.561	105.533	0.026
140.791	105.691	105.771	-0.075
141.105	105.927	106.002	-0.070
142.276	106.859	106.863	-0.004
156.302	117.173	117.183	-0.008
157.729	118.422	118.232	0.159

TABLE 6-1 - Continued

Eykman Molecular Refraction	Molecular Weight	Calculated Molecular Weight	Per Cent Deviation
170.378	127.499	127.539	-0.031

Average error = 0.000 per cent

Average absolute error = 0.055 per cent

EMR = 2.185 + 0.7357 MW

MW = - 2.970 + 1.3591 EMR

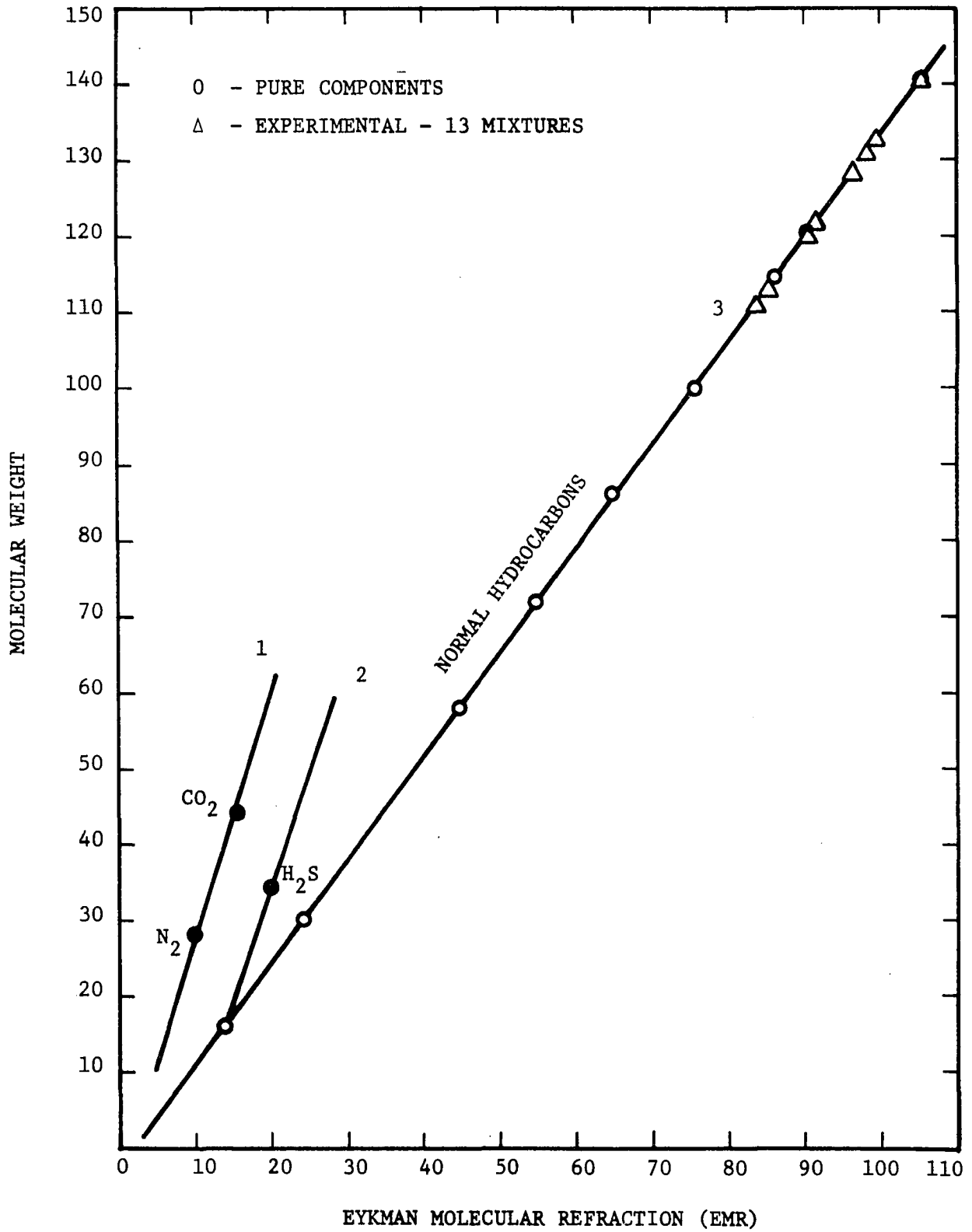


FIGURE 6-2. CORRELATION OF MOLECULAR WEIGHT AND EMR

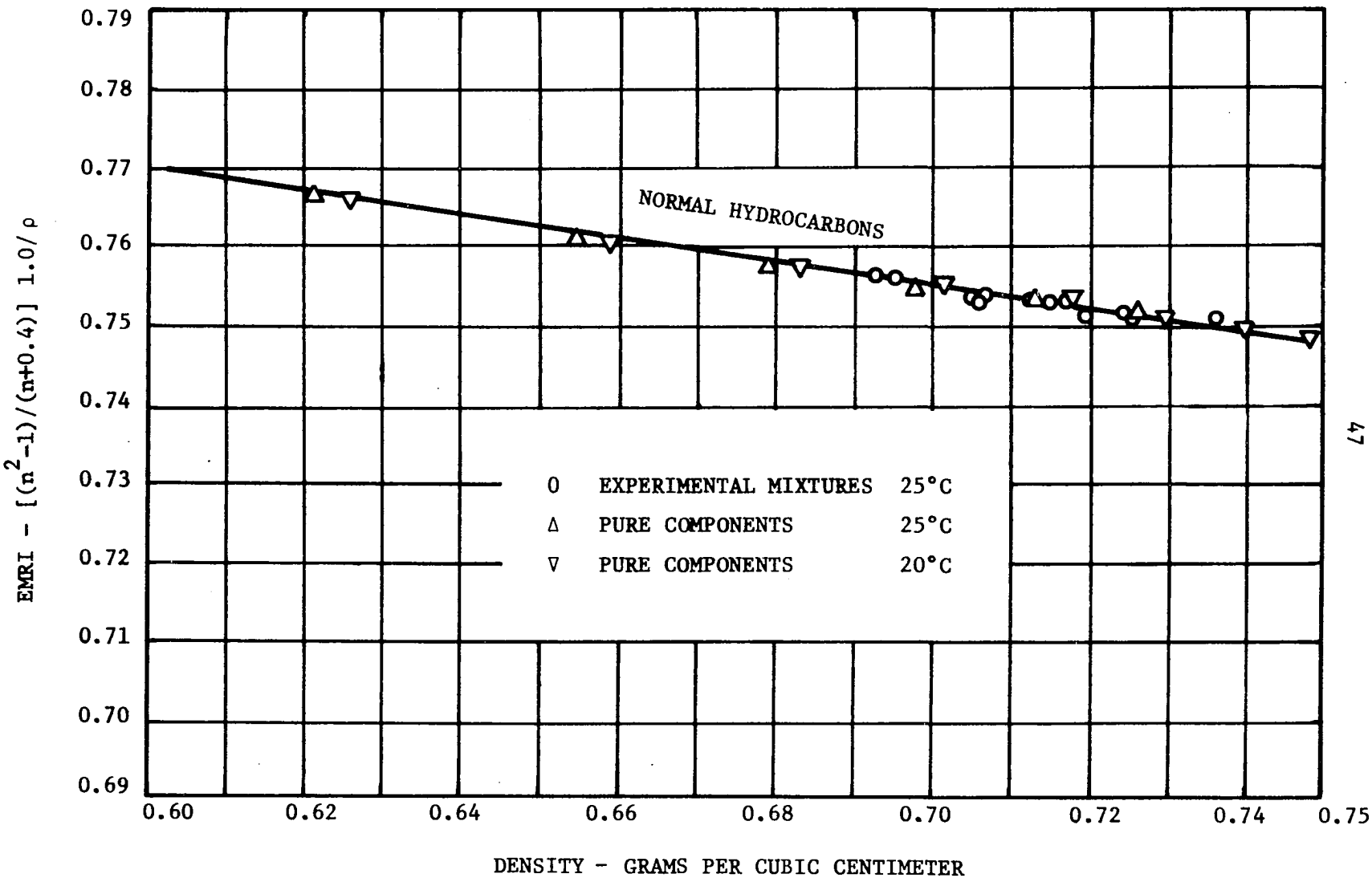


FIGURE 6-3. CORRELATION OF EYKMAN REFRACTIVE INTERCEPT AND DENSITY

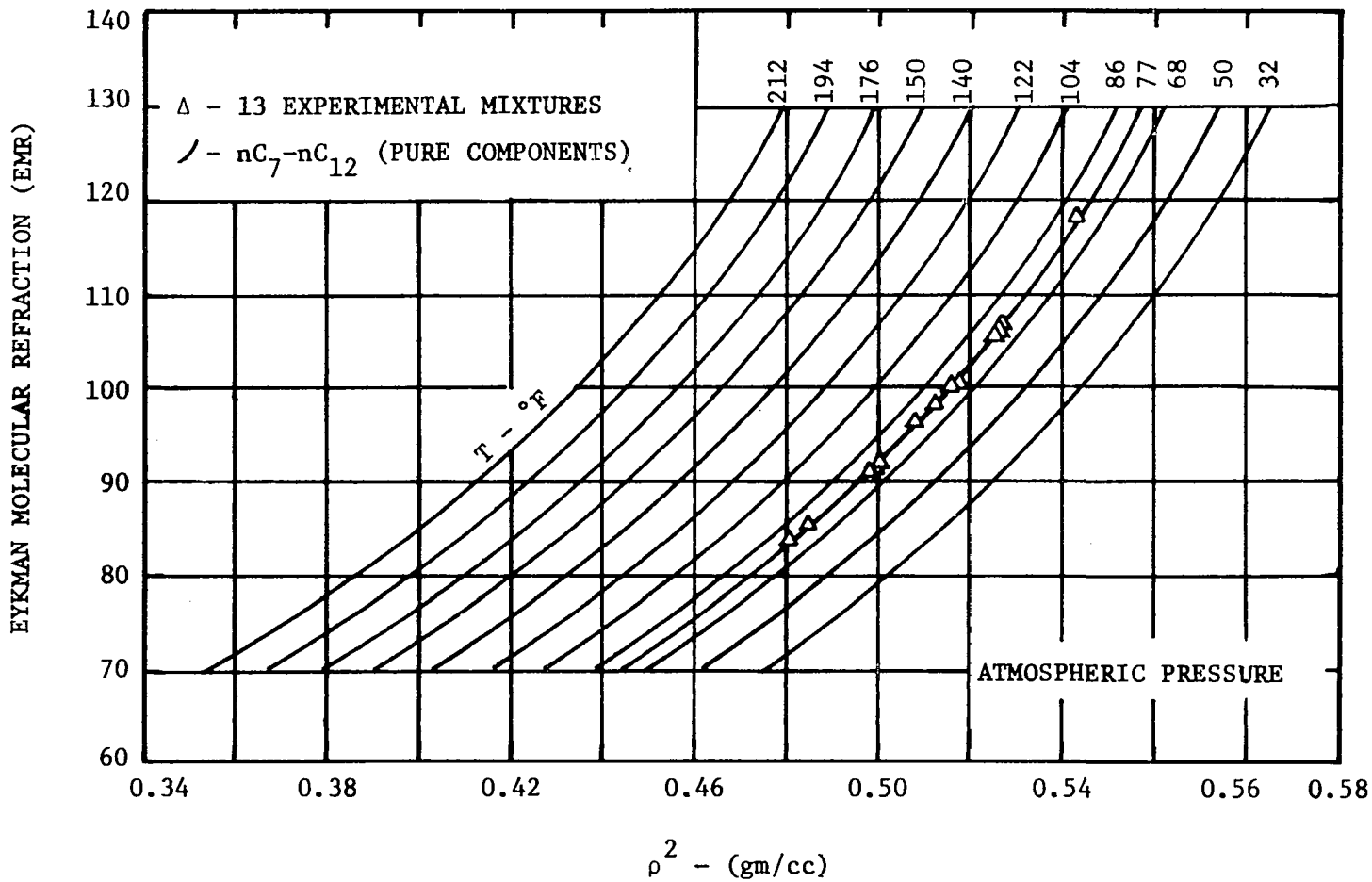


FIGURE 6-4. EYKMAN MOLECULAR REFRACTION (EMR) VERSUS ρ^2

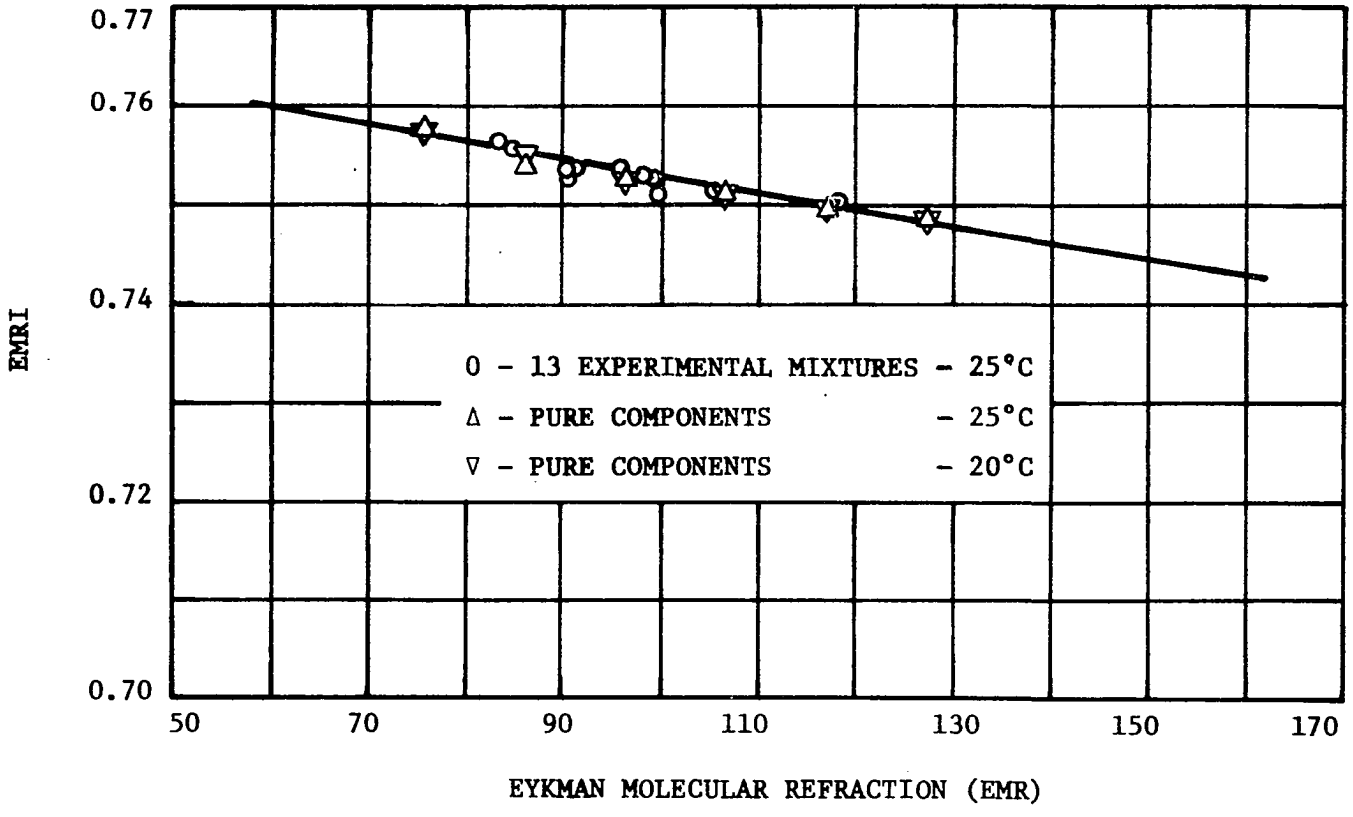


FIGURE 6-5. EYKMAN REFRACTIVE INTERCEPT VERSUS EMR.

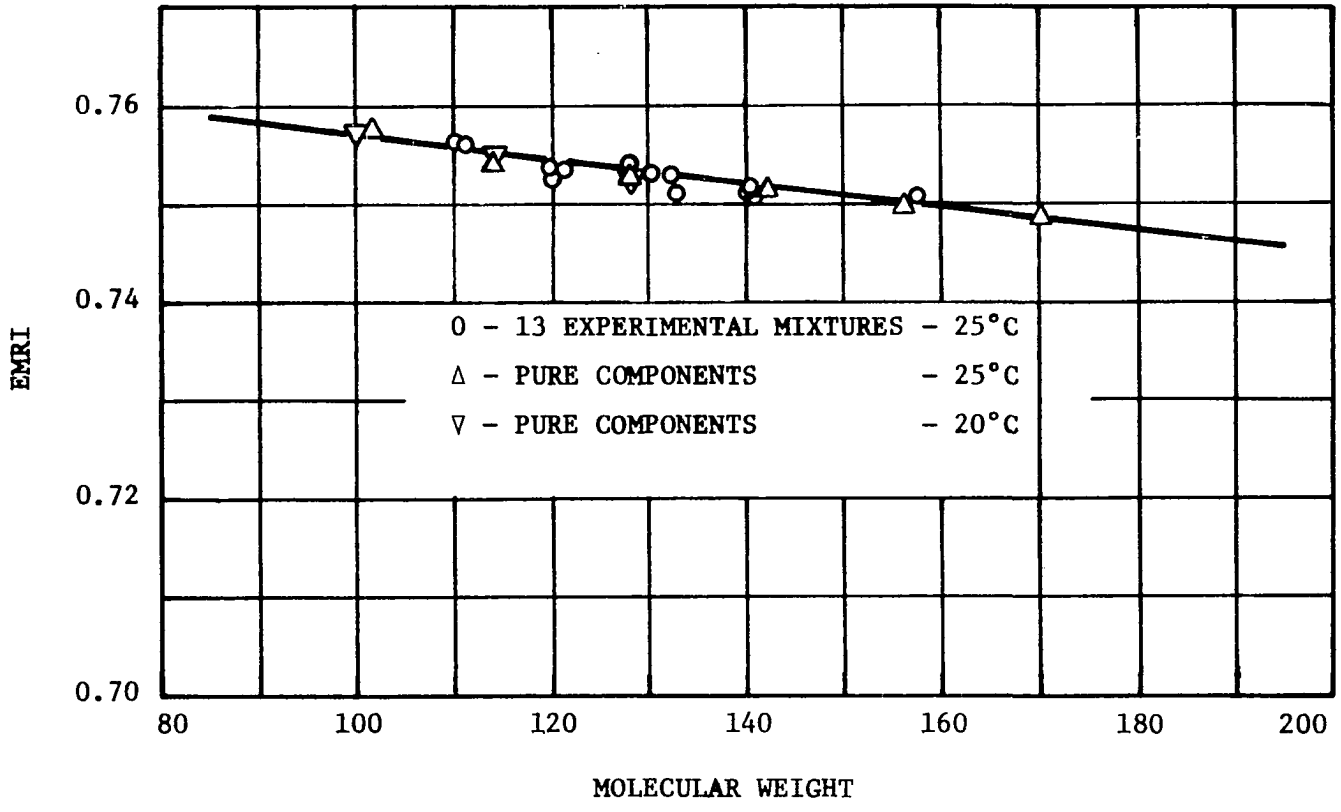


FIGURE 6-6. EYKMAN REFRACTIVE INTERCEPT VERSUS MOLECULAR WEIGHT

CHAPTER VII

CONSTRUCTION PROCEDURE FOR COMPRESSIBILITY CHARTS

The many advantages of using molecular refraction as a third parameter dictated an investigation of its use in predicting the compressibility of gas mixtures. This necessarily required construction of a new set of charts and the formulation of new combination or mixing rules.

Experimental data from twenty-five mixtures* were used to construct the charts. The ranges of pressures and temperatures studied were between 15 psia to 7000 psia and 40°F to 175°F, respectively; a total of 598 pressure points at sixty-one temperature conditions. Table 7-1 shows the ranges of non-hydrocarbon content of the mixtures studied. A more detailed tabulation of the mixtures studied can be found in Appendix E.

A. Compressibility Chart No. 1

First plots of the ratio of critical temperature to critical pressure and the ratio of critical temperature to the square root of critical pressure versus EMR were constructed. (Figures 7-1 and 7-2, respectively.)

*See References (9), (11), (104), (105) and (137).

Each mixture was split up into a pseudo binary. Methane, along with the other non-hydrocarbons (N_2, CO_2, H_2S, etc.) formed one group of the binary and the remaining hydrocarbons (C^+_2) formed the other. The additive EMR for each group was determined and a critical temperature and pressure of each mixture was determined graphically. A sample calculation is shown in Appendix L.

Reduced temperatures and pressures for the 61 temperature and 598 pressure points were calculated. At each reduced temperature condition a spline curve routine was used to define the curve of experimental compressibility factors versus reduced pressures at selected reduced pressures (1714 pressure points). The spline curve is a piecewise continuous cubic polynomial through the given points preserving continuity of the first and second derivatives.

Starting from a reduced pressure of 1.00 and increasing in increments of 0.5, the best least squares fit of experimental compressibility factor versus reduced temperatures at constant reduced pressures were carried out. The constants obtained were used to carry out an error analysis of the calculated compressibility factors versus true experimental factors. In no case did the average error of the average absolute error exceed 0.23 and 3.55 per cent, respectively. Table 7-2 gives a more detailed account.

Figure 7-3, appropriately labelled compressibility chart number 1, is the end result of this approach.

B. Compressibility Chart No. 2

In this approach the pseudo critical temperature was obtained similar to Kay's method, i.e.:

TABLE 7-1

NONHYDROCARBON CONTENT OF MIXTURES STUDIED

Components	No. of Mixtures	Ranges of Nonhydrocarbon Mol Per Cent
C_nH_{2n+2}	6	-
$C_nH_{2n+2} + N_2$	3	N_2 = 3.75 - 7.50
$C_nH_{2n+2} + CO_2$	4	CO_2 = 0.40 - 12.92
$C_nH_{2n+2} + H_2S$	5	H_2S = 4.70 - 19.70
$C_nH_{2n+2} + N_2 + CO_2$	4	N_2 = 0.52 - 0.81 CO_2 = 1.80 - 20.16
$C_nH_{2n+2} + N_2 + CO_2 + H_2S$	3	N_2 = 0.46 - 0.52 CO_2 = 0.30 - 1.31 H_2S = 5.70 - 22.60

$$\sum_{i=1}^{\hat{n}} X_i T_{c_i} = T^*_c \qquad (7\text{-}1)$$

However, the pseudo critical pressure was obtained graphically from a plot of the ratio of critical temperatures to critical pressures versus EMR, as seen in Figure 7-1. In order to determine T_c/P_c from Figure 7-1, the same binary approach utilized in method 1 was adopted. A sample calculation is given in Appendix L.

After calculating the reduced pressures and temperatures, the curve fitting routine was similar to that used in the construction of compressibility chart number one.

In this method, up to and including a reduced pressure of 6.50, the average error was slightly greater than method one, while the average absolute error was less. However, from a reduced pressure of 7.00, both the average error and the average absolute error were greater than the previous method. The results of the error analysis are tabulated in Table 7-2. Here it is seen that the maximum average error and maximum average absolute error were -9.88 and 9.89 per cent, respectively, at a P_R of 7.00. The compressibility chart constructed by this approach is shown in Figure 7-4.

C. Compressibility Chart No. 3

In this method it is suggested that the simple spherical non-polar molecules with the exception of methane be grouped together; ethane plus hydrocarbons forming a second group, while methane and polar molecules form a third group. The reason for grouping methane with other polar molecules is as follows. Due to the tightness of its

electronic shell (brought on by the symmetric distribution of adjacent positive charges), methane shows abnormally low refraction in comparison to the other members of the normal paraffin series. That is, the difference between the EMR of ethane and methane is too low in comparison to the difference between any other two consecutive members of the paraffin series. Therefore it was decided not to correlate methane with the ethane plus.

Moreover, it was found that, depending on the parameters to be correlated, the EMR value of methane correlated best with those of polar compounds; hence, the particular grouping.

A mixture containing two of the three types of molecules will be a pseudo binary while one containing all three types will be a pseudo ternary.

Satter in his studies had developed a dimensionless parameter, F, which depends on the characteristics of the molecular species.

$$F = \frac{hP_c^{1/3}}{(kT_c)^{5/6}\sqrt{m}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7\text{-}2)$$

where, h = Plank's constant

m = mass of a single molecule

k = Boltzmann's constant

T = temperature

kT = energy per molecule

Equation (7-2) can be written conveniently as,

$$F = 5.665\, P_c^{1/3}/(T_c)^{5/6}\,(MW)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7\text{-}3)$$

where, P_c = critical pressure - psi

T_c = critical temperature - °R

MW = molecular weight

Plots of χ - the reciprocal of Satter's dimensionless function F - versus EMR and the ratio of critical temperature to critical pressure raised to the one third power (Figures 7-7 and 7-8, respectively) were used to obtain reduced temperatures and pressures. The actual construction of the chart was similar to the previous ones.

Figure 7-5 is the resulting compressibility chart. An error analysis similar to that used in the previous methods was carried out on the points used in the plot of this compressibility chart. The maximum average error and average absolute error of -5.21 and 13.96 per cent occurred at a reduced pressure of 7.50. A glance at the tabulated results of the error analysis, shown in Table 7-2, would reveal that, from a reduced pressure of 5.00, the average absolute error was in excess of 10.00 per cent and increased thereon.

A sample calculation utilizing this method can be found in Appendix L.

D. Compressibility Chart No. 4

The grouping adopted in Method 3 is also used in this method. Again use is made of Figure 7-7; however, instead of Figure 7-8 - the plot of the ratio of critical temperature to critical pressure raised to the one third power versus EMR - Figure 7-9 - a plot of critical temperature versus EMR, was used.

The end results of this approach is appropriately labeled "Compressibility Chart Number 4" (Figure 7-5). As in previous cases,

an error analysis of the points plotted was carried out. The maximum average error and average absolute error were 1.96 and 4.93 per cent, respectively, and occurred at a reduced pressure of 6.50. The results of the error analysis of this method can be found in Table 7-2, and a sample calculation in Appendix L.

Figures 7-10 and 7-11 are sample curves for the various methods showing the scatter in the raw data at a reduced pressure of 2.0. These curves should not be compared since a value of $P_R = 2.0$ would be different for each compressibility chart.

On the basis of the error analysis tabulated in Table 7-2, there is little to choose between methods one and four. However, because of the simpler calculation procedure involved, method one is recommended over method four.

E. Procedure for the Application of Proposed Method

1. Divide the mixture into two groupings, i.e.:

   Group 1 - Methane, carbon dioxide, hydrogen sulphide, nitrogen;

   Group 2 - Ethane plus hydrocarbons.

2. If heptanes plus are present, then from a liquid density measurement at any temperature, go to Figure 6-4 for a value of EMR. Figures 6-3, 6-5 and 6-6 can also be utilized for obtaining EMR from density.

3. For each grouping in the pseudo binary calculate EMR;

$$EMR_1 = (X_i^*)(EMR)_i$$

$$EMR_2 = (X_i^*)(EMR)_i$$

4. With $(EMR)_1$ obtain $(T_c/P_c)_1$ for Group 1 from curve 1 in Figure 7-1 and with $(EMR)_2$ obtain $(T_c/P_c)_2$ for Group 2 from curve 2 in Figure 7-1.

$$T_c/P_c = (X_i)(T_c/P_c)_i + (X_j)(T_c/P_c)_2$$

5. Obtain $(EMR)_{mix}$. This can be obtained by two methods:

   (a) Before step one

$$(EMR)_{mix} = \sum_{i=1}^{\hat{n}} X_i \, (EMR)_i$$

   (b) After step one

$$(EMR)_{mix} = \sum_{i=1}^{\hat{n}} X_i \, (EMR_1) + X_j \, (EMR_2)$$

6. With a value of $(EMR)_{mix}$ go to Figure 7-2 and read off $T_c/\sqrt{P}_c$.

7. With values for T_c/P_c and $T_c/\sqrt{P}_c$ solve for T_c and P_c.

8. $P_R = P/P_c$

   $T_R = T/T_c$

9. From the generalized compressibility chart for this method (Figure 7-3), read off values of Z for a given P_R and T_R.

TABLE 7-2

ERROR DISTRIBUTION

Compressibility Chart

PR	Method 1			Method 2			Method 3			Method 4		
	Number of Z's Considered	Average Error %	Average Absolute Error %	Number of Z's Considered	Average Error %	Average Absolute Error %	Number of Z's Considered	Average Error %	Average Absolute Error %	Number of Z's Considered	Average Error %	Average Absolute Error %
1.00	23	0.18	2.72	25	0.40	1.96	17	-1.55	1.73	34	-0.19	1.59
1.50	50	0.19	2.81	54	0.43	2.62	52	-0.49	2.65	61	0.57	1.78
2.00	50	0.18	3.01	54	-2.92	3.64	52	0.80	4.26	64	1.26	2.51
2.50	50	0.23	3.34	54	0.85	3.01	52	0.37	5.63	64	0.79	2.84
3.00	50	0.22	3.54	54	1.96	2.99	52	0.13	6.11	64	0.64	3.42
3.50	50	0.20	3.55	54	0.50	2.30	52	0.77	7.45	64	1.28	3.64
4.00	47	0.15	3.20	54	0.73	2.02	52	1.17	8.76	64	0.66	3.74
4.50	44	0.13	3.12	54	0.39	1.74	52	0.83	9.85	64	0.56	3.87
5.00	40	0.15	3.17	54	0.49	1.63	52	1.70	10.62	64	0.65	4.04
5.50	34	0.21	2.82	54	0.17	1.63	52	1.35	11.09	64	1.06	3.80
6.00	32	0.17	2.57	54	-0.21	1.99	52	2.06	11.46	64	0.47	3.80
6.50	32	0.03	2.30	49	0.18	1.74	50	1.54	10.68	64	1.96	4.93
7.00	30	-0.08	2.44	39	-9.88	9.89	53	2.27	13.22	44	0.97	4.57
7.50	25	0.20	1.92	33	-3.09	3.14		-5.21	13.96	43	-1.85	4.23

Values lower than T_R = 1.0 are not included in the error analysis.

Average error = $(\Sigma((Z-Z_{calc})/Z)*100)/$number of points.

Average absolute error = $|\Sigma((Z-Z_{calc})/Z)*100|/$number of points.

F. Mixing Rule

In order to construct any generalized compressibility chart, it is necessary to formulate a mixing rule (or combination rule) to arrive at the characteristic properties of mixtures. A combination rule is merely a method of combining the values of the interaction constants from the corresponding constants of the pure gases.

In the development of these mixing rules (pseudo-critical treatment) for the common semi-empirical equations of state, the most used schemes for combining the interaction constants are:

$$\bar{a}_{ij} = \frac{1}{2}\left[\bar{a}_{ii} + \bar{a}_{jj}\right] \quad \text{- linear combination} \tag{7-4}$$

$$\bar{a}_{ij} = \bar{a}_{ii}^{1/2}\,\bar{a}_{jj}^{1/2} \quad \text{- square root combination} \tag{7-5}$$

$$\bar{a}_{ij} = \left[\frac{\bar{a}_{ii}^{1/3} + \bar{a}_{jj}^{1/3}}{2}\right]^3 \quad \text{- Lorentz combination} \tag{7-6}$$

where,

$\bar{a}$ = any constant in the semi-empirical equations of state.

In the case of the virial equation, the combining of the interaction constants is accomplished by the following rules:

$$\sigma_{if} = 1/2\ (\sigma_{ii} + \sigma_{jj}) \tag{7-7}$$

$$\hat{\varepsilon}_{ij} = (\hat{\varepsilon}_{ii}\,\hat{\varepsilon}_{jj})^{1/2} \tag{7-8}$$

where,

σ_{ij} = separation between a molecule of the ith kind and the jth kind.

$\hat{\varepsilon}_{ij}$ = potential energy between a molecule of ith kind and the jth kind.

A summary of the more popular pseudocritical or combination rules are shown in Table H1 of Appendix H. These combination rules were developed for non-polar gases and gas mixtures and, as a rule, have been used satisfactorily on light hydrocarbon systems in conjunction with Katz's generalized compressibility charts.

If one were to examine the composition data for the gas mixtures shown in Appendix F, and then compare the tabulated pseudocritical pressures and temperatures for the various methods shown in Appendix H, one would observe that for the light hydrocarbon mixtures there is trivial differences between the various methods. However, for mixtures containing complex hydrocarbons (heptanes plus) or polar compounds, the differences between the calculated pseudocritical values of the various methods get greater as the mixtures become more complex.

In an effort to improve the applicability of the various "rules" to complex mixtures, various investigators have applied corrections to the critical constants of the "offending" components. In practice, these corrections work well only for the mixtures from which they were generated. It is reasonable to conclude that the existing two parameter pseudocritical approaches cannot adequately account for the complexity of effects brought about by intermolecular forces between molecules of different sizes and molecular structure - as in a hydrocarbon mixture containing heptanes plus fractions along with H_2S, CO_2 and N_2.

In this work, on the basis of structure and optical properties, each mixture was arbitrarily divided into groups. The relationship between the critical properties of the pure components of each group and the Eykman Molecular Refraction formula, constituted the mixing rule approach.

Figures 7-1, 7-2, 7-7 and 7-8 are graphical solutions of the various mixing rules tried in this study. Figures 7-1 and 7-2 are the recommended combinations to be used in conjunction with Method 1.

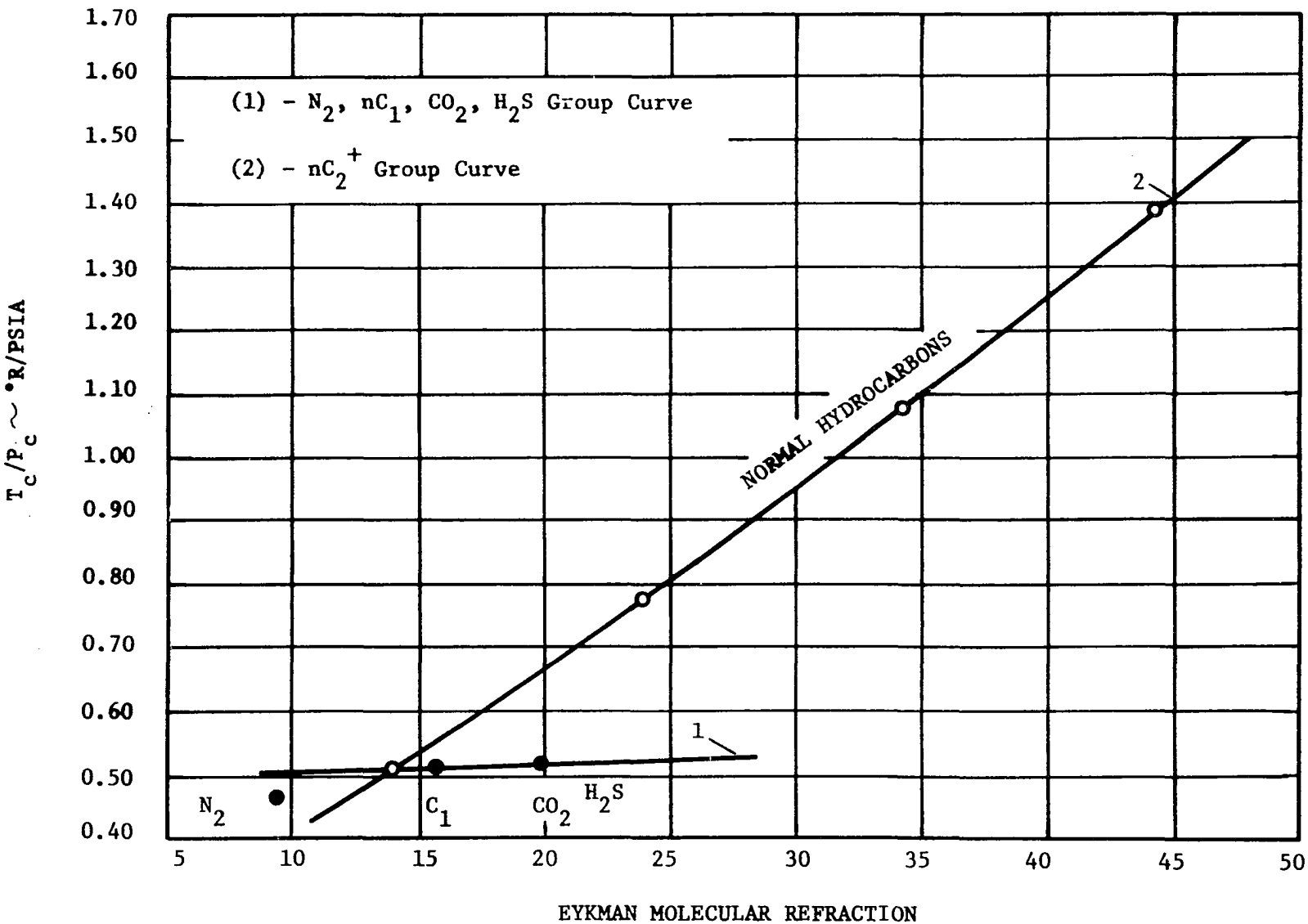


FIGURE 7-1. CORRELATION OF T_c/P_c AND EMR

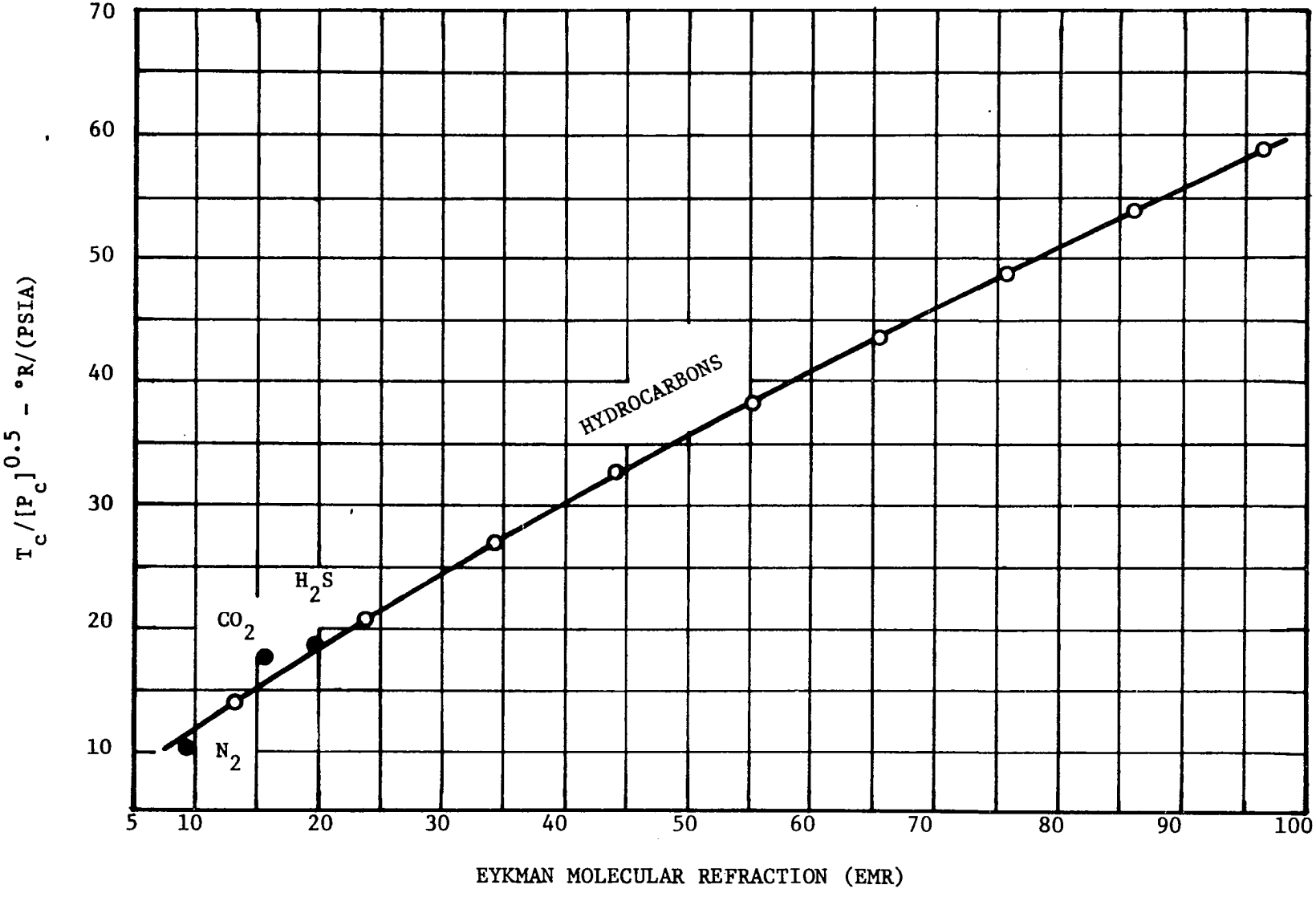


FIGURE 7-2. CORRELATION OF $T_c/[P_c]^{0.5}$ AND EMR

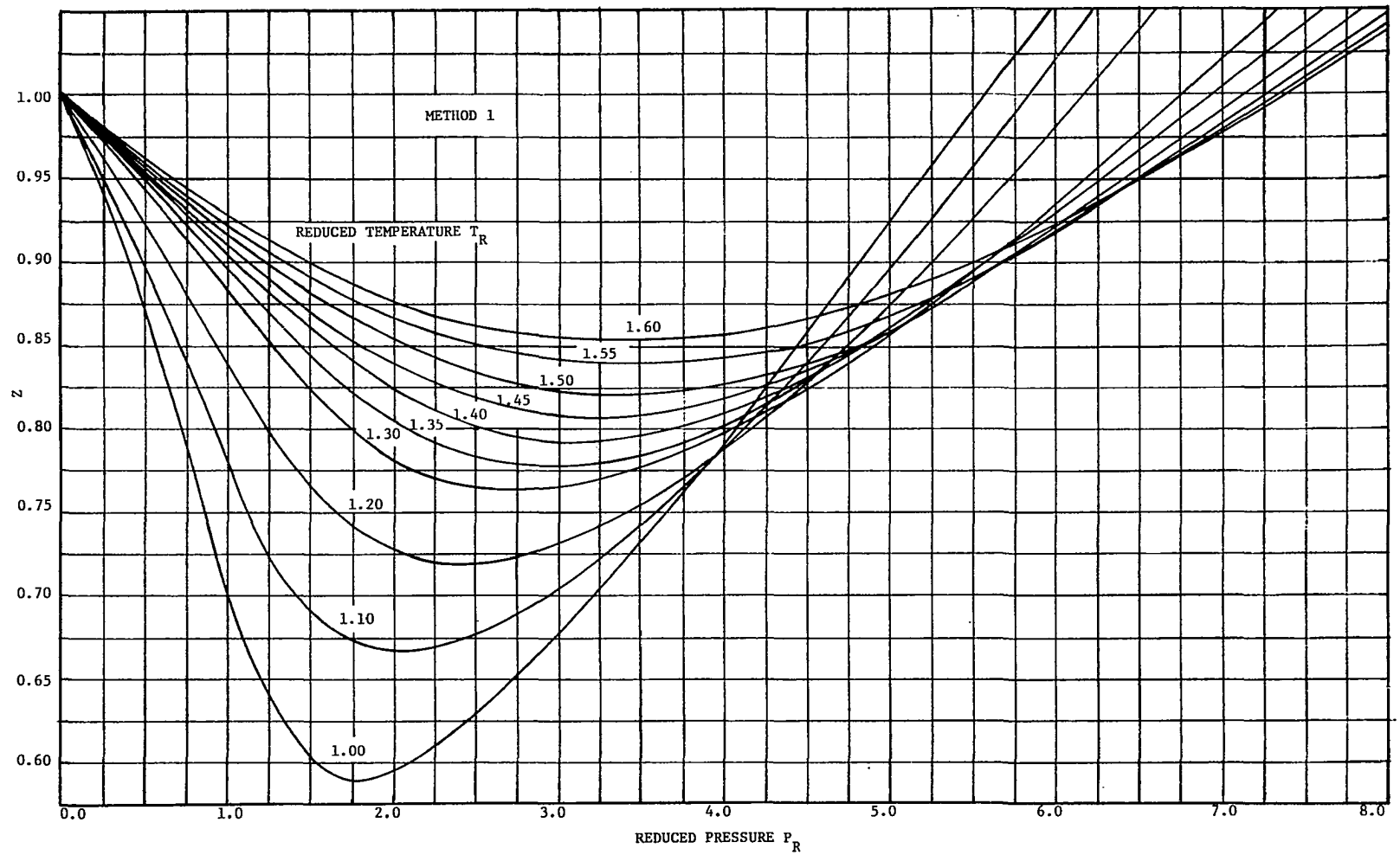


FIGURE 7-3. GENERALIZED COMPRESSIBILITY FACTOR Z AT REDUCED TEMPERATURES AND PRESSURES

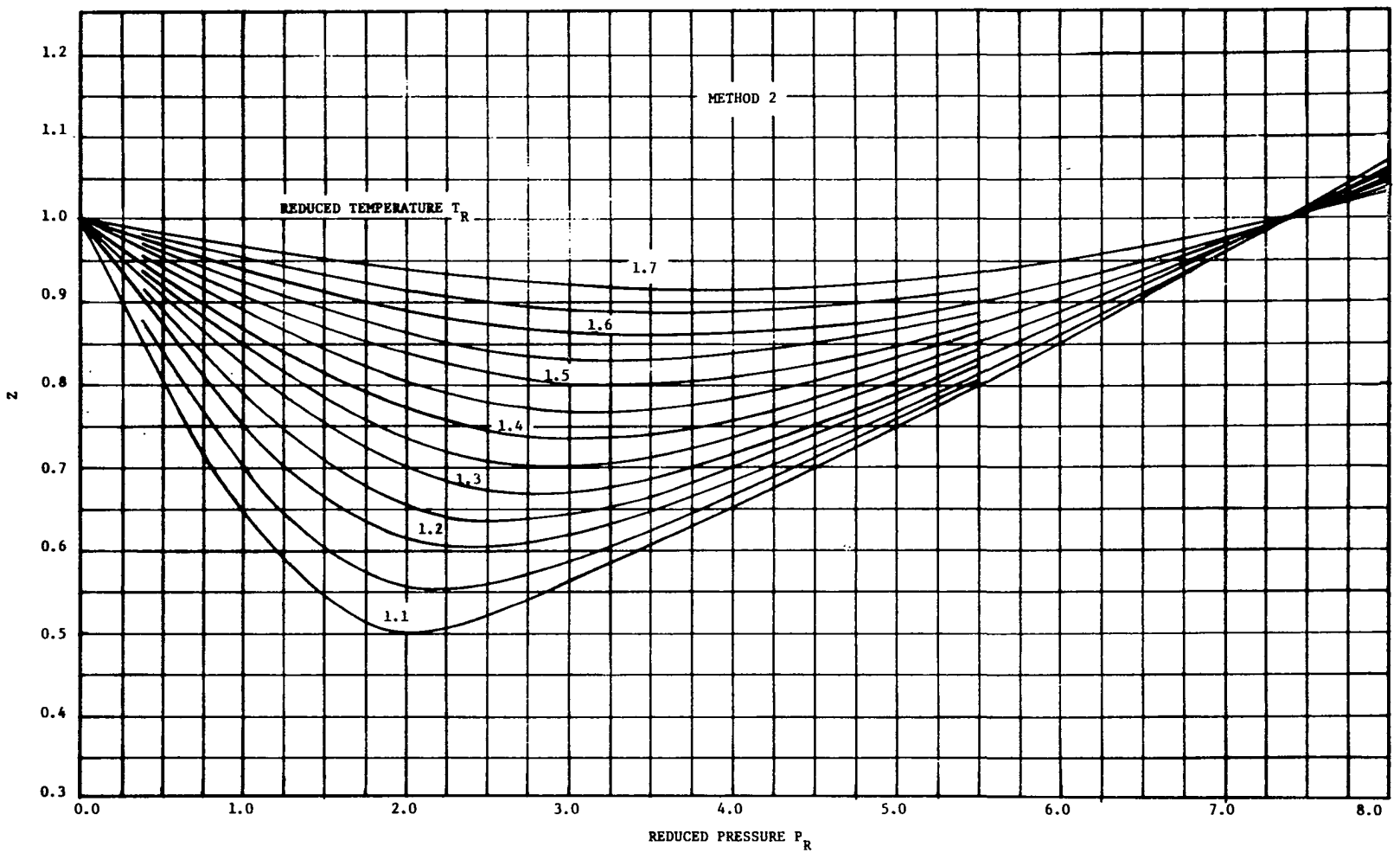


FIGURE 7-4. GENERALIZED COMPRESSIBILITY FACTOR Z
AT REDUCED TEMPERATURES AND PRESSURES

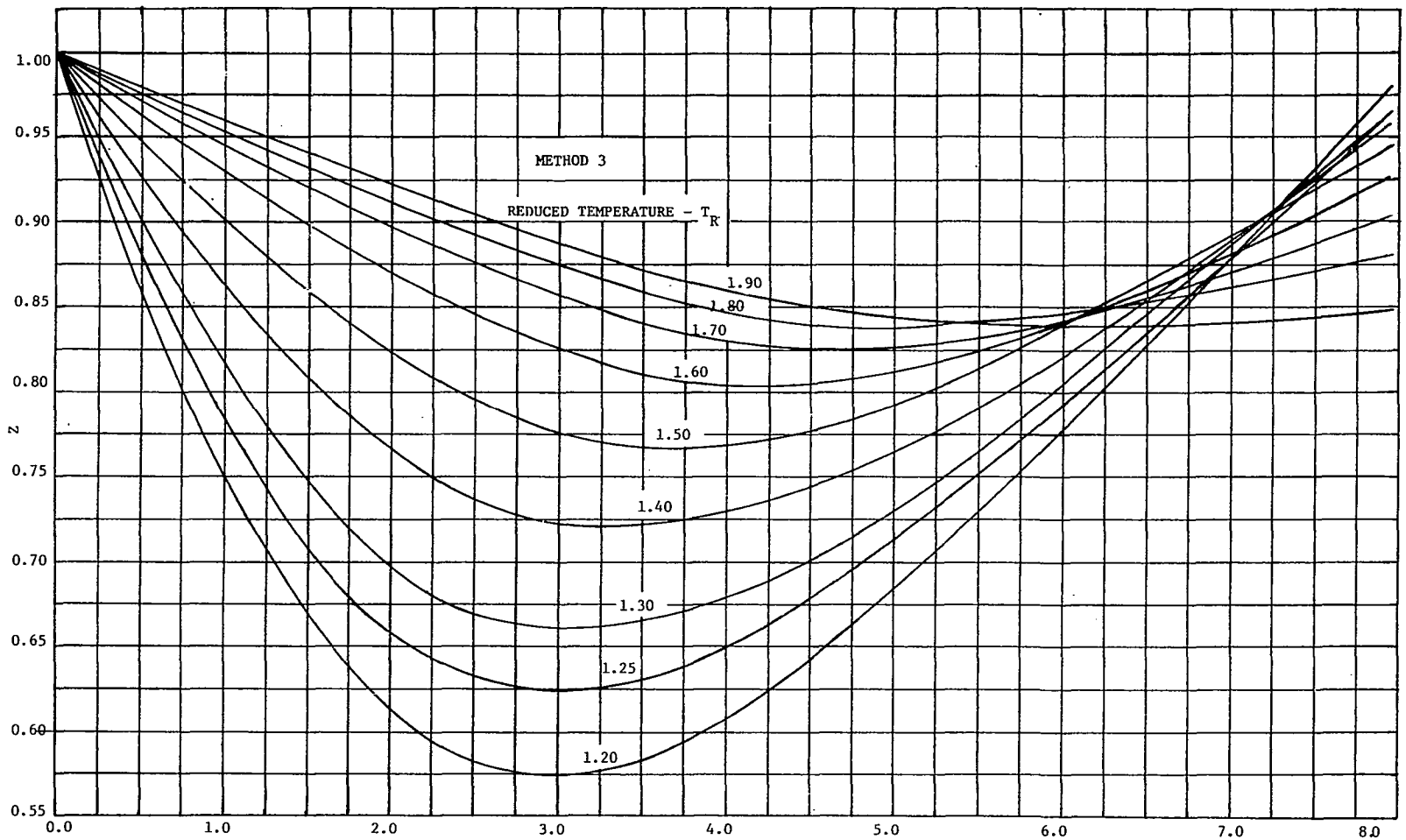


FIGURE 7-5. GENERALIZED COMPRESSIBILITY FACTOR Z
AT REDUCED TEMPERATURES AND PRESSURES

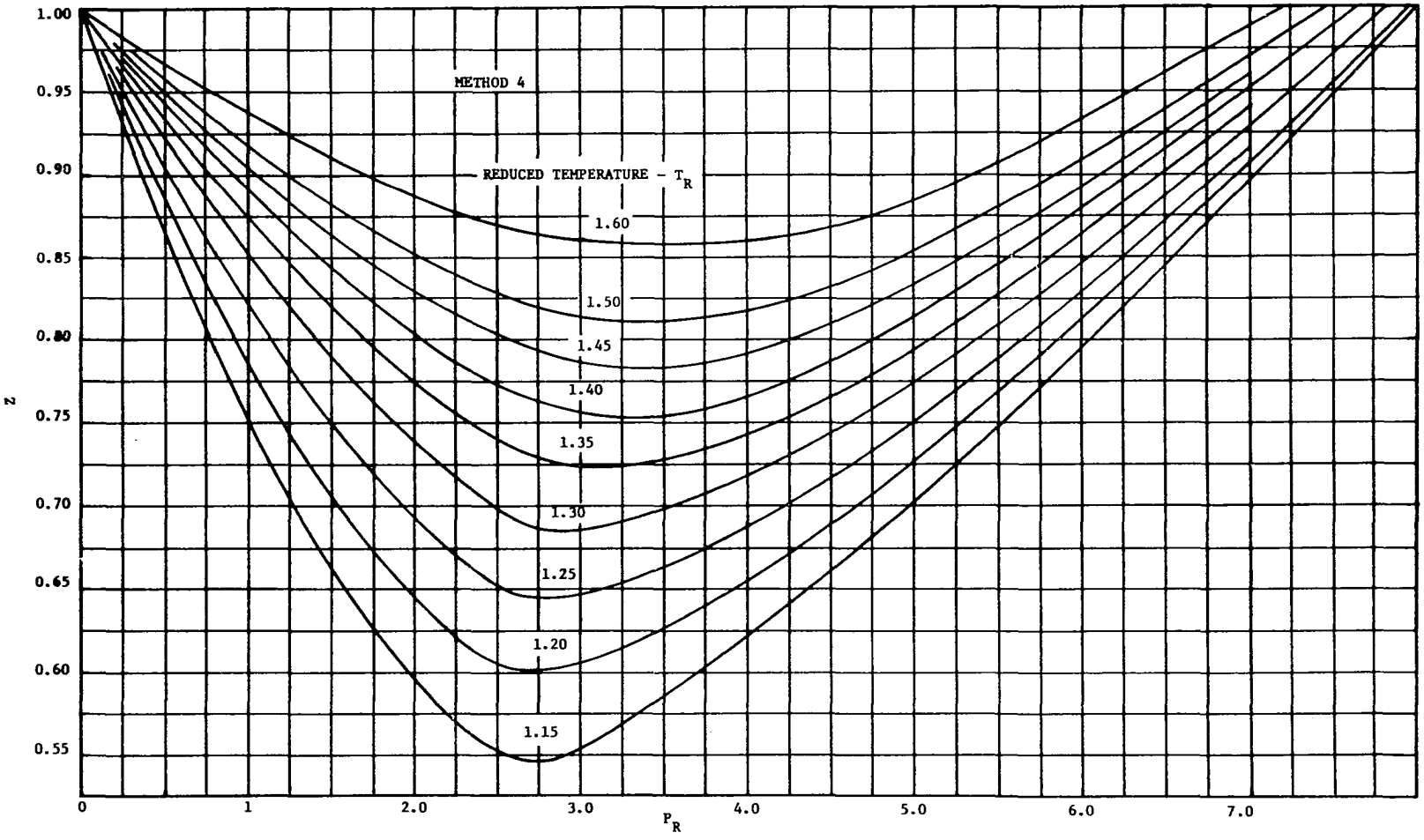


FIGURE 7-6. GENERALIZED COMPRESSIBILITY FACTOR Z AT REDUCED TEMPERATURES AND PRESSURES.

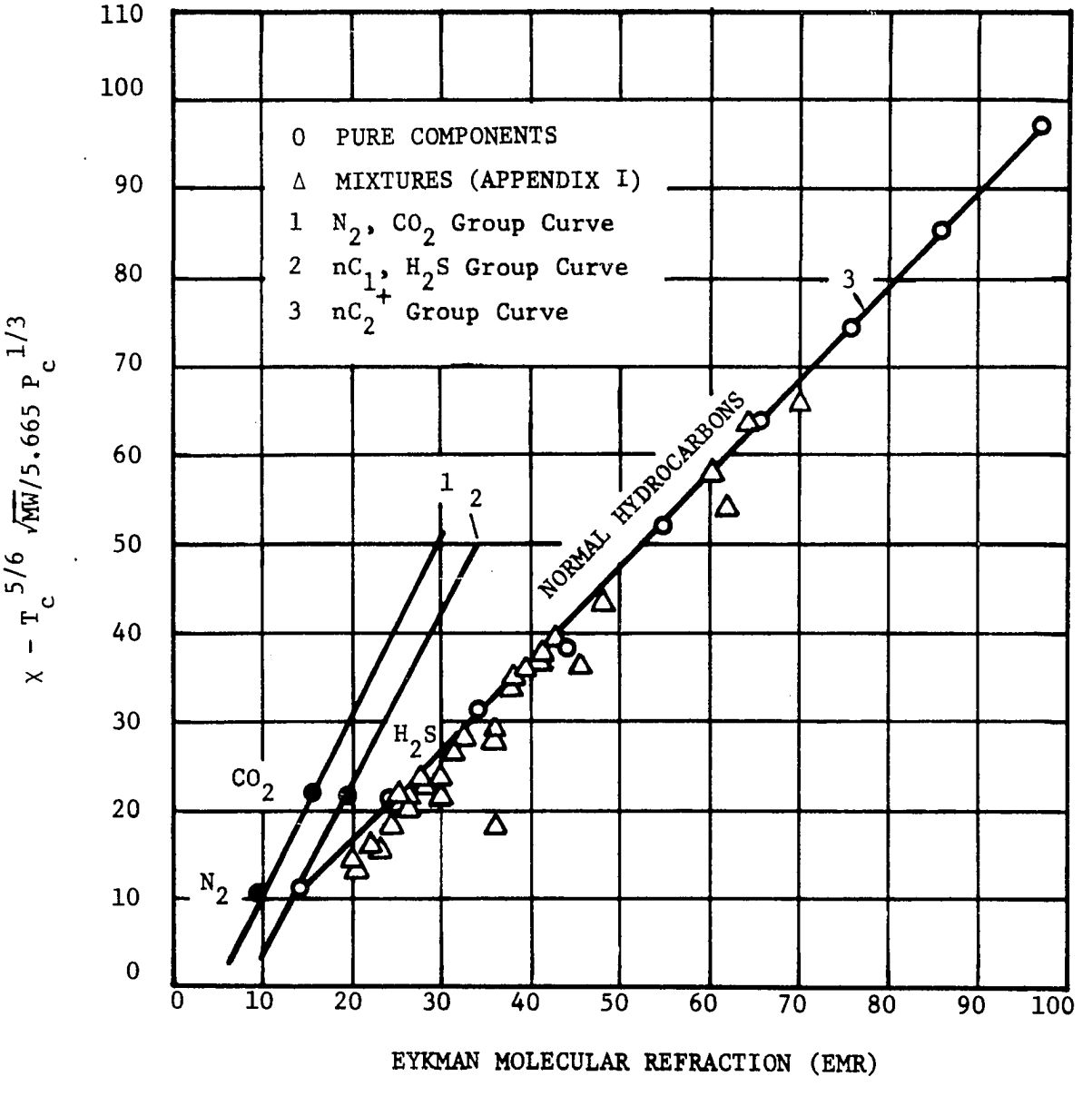


FIGURE 7-7. χ VERSUS EMR

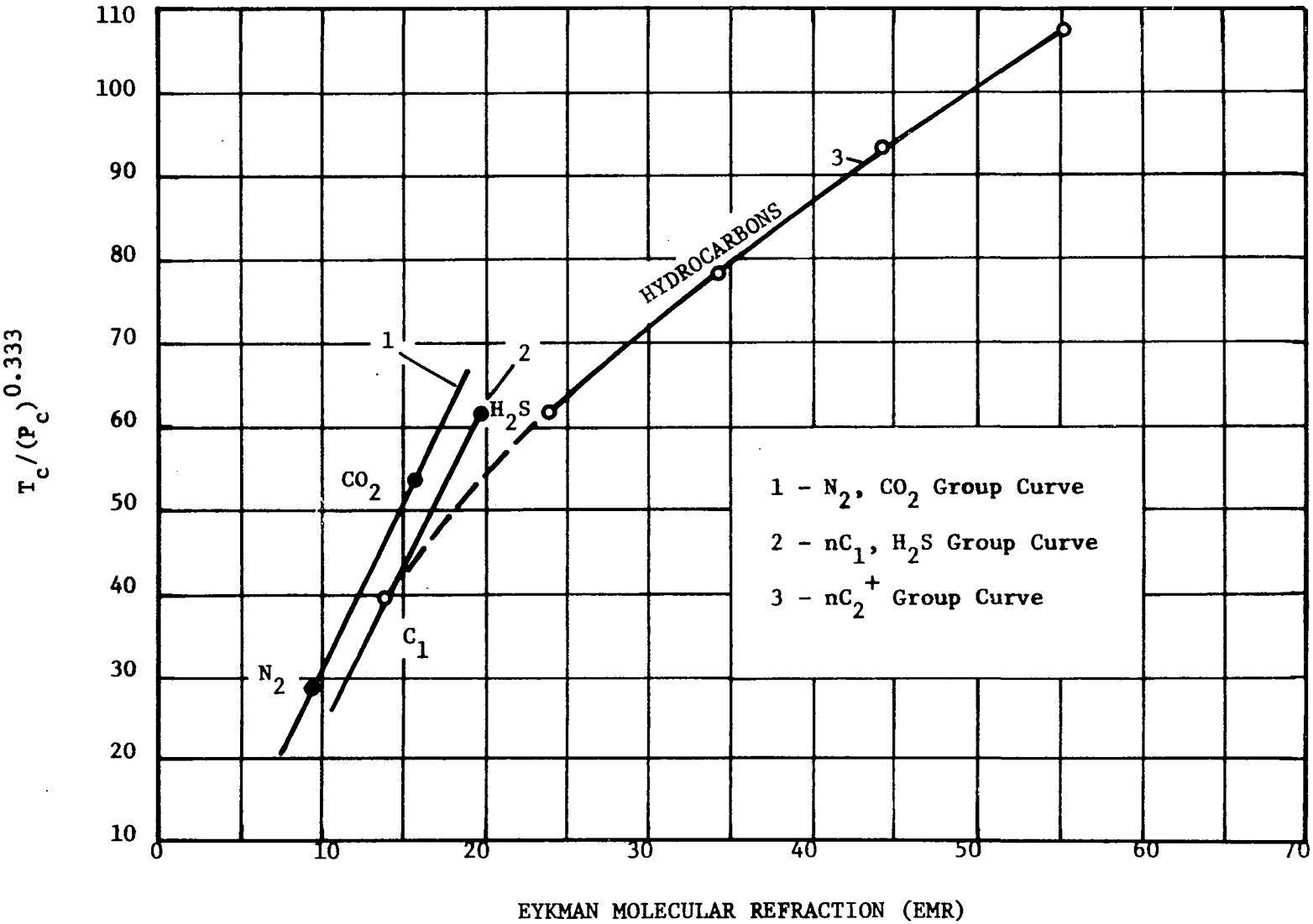


FIGURE 7-8. $T_c/P_c^{0.333}$ VERSUS EYKMAN MOLECULAR REFRACTION

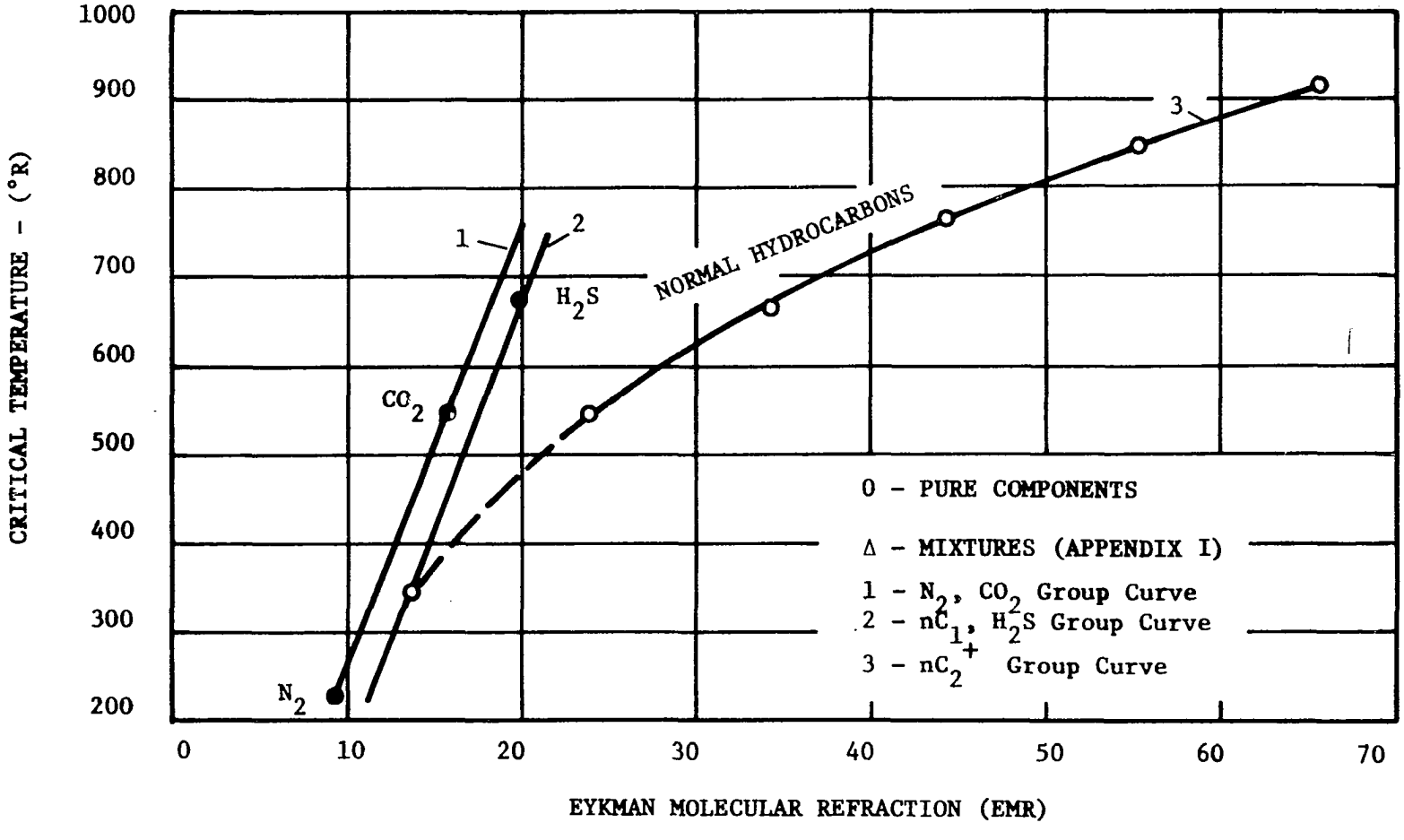
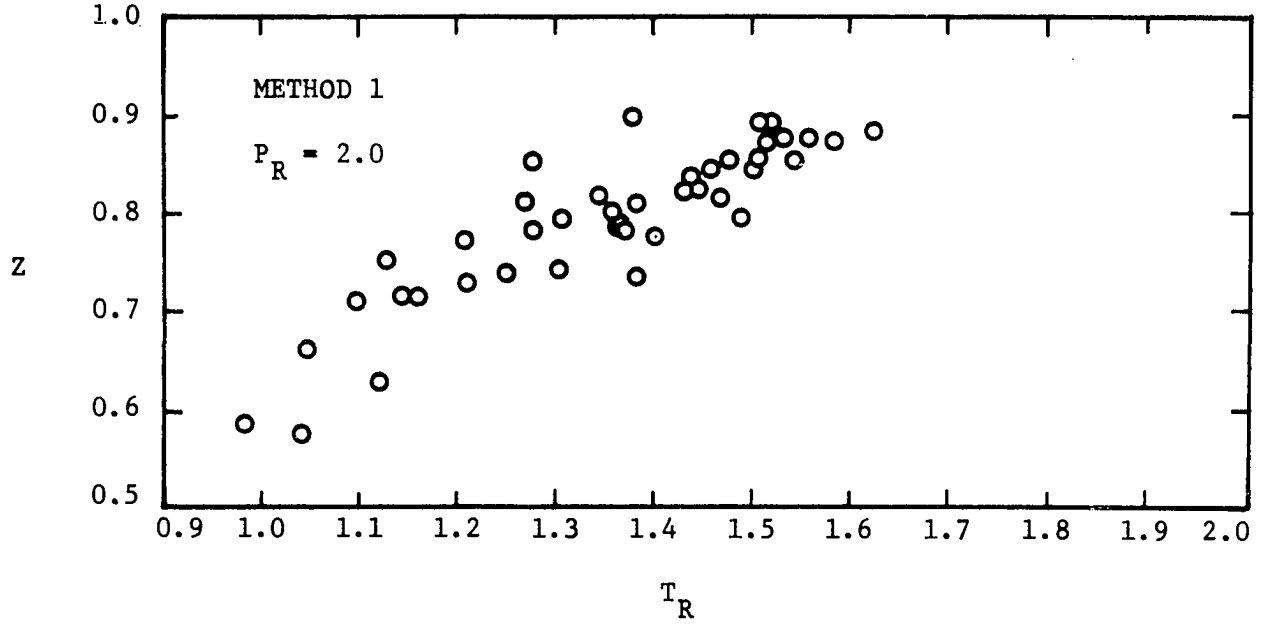


FIGURE 7-9. CRITICAL TEMPERATURE (°R) VERSUS EMR.



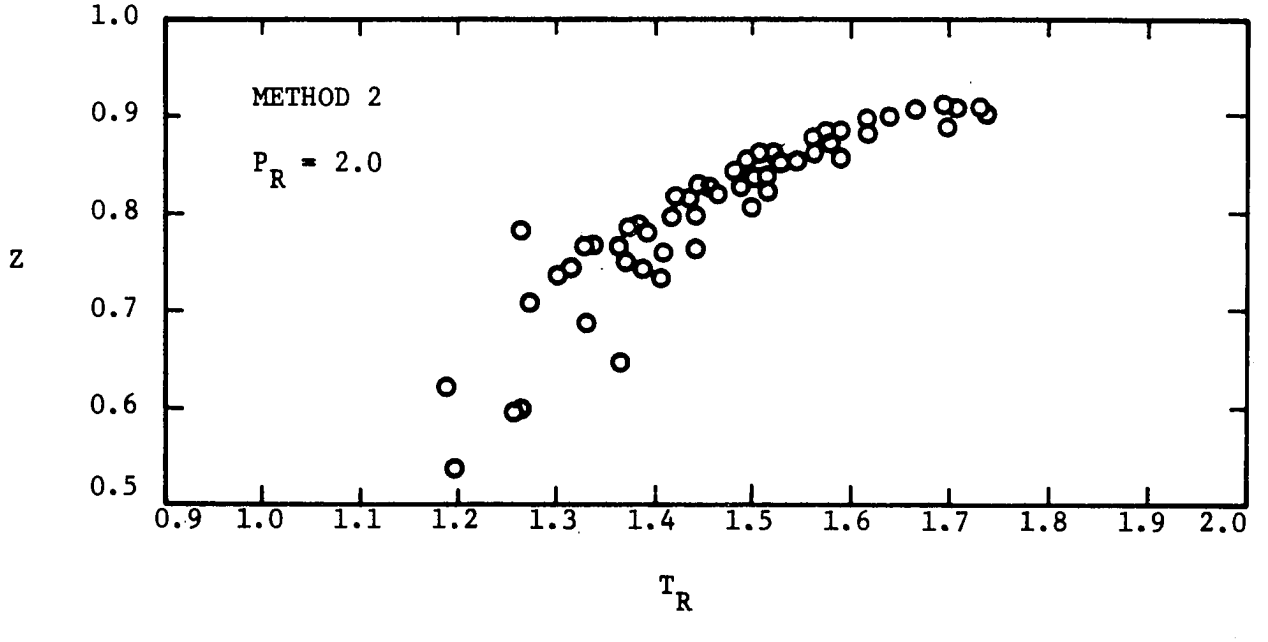
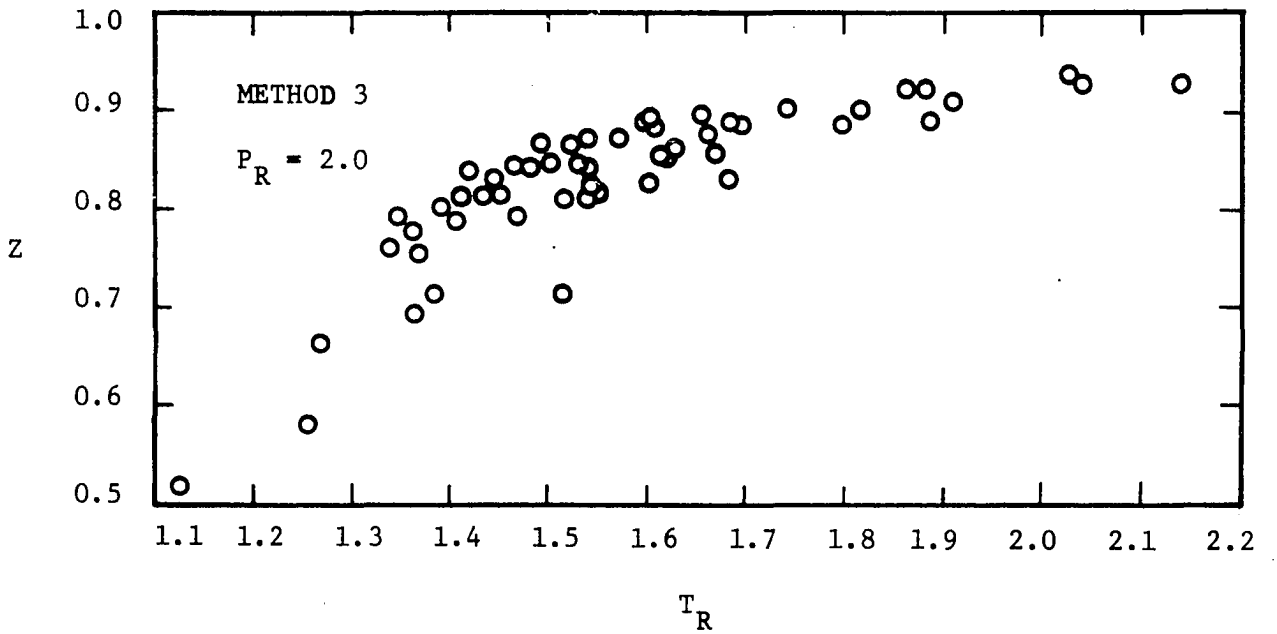


FIGURE 7-10. COMPRESSIBILITY FACTOR VERSUS REDUCED TEMPERATURE AT P_R = 2.0.



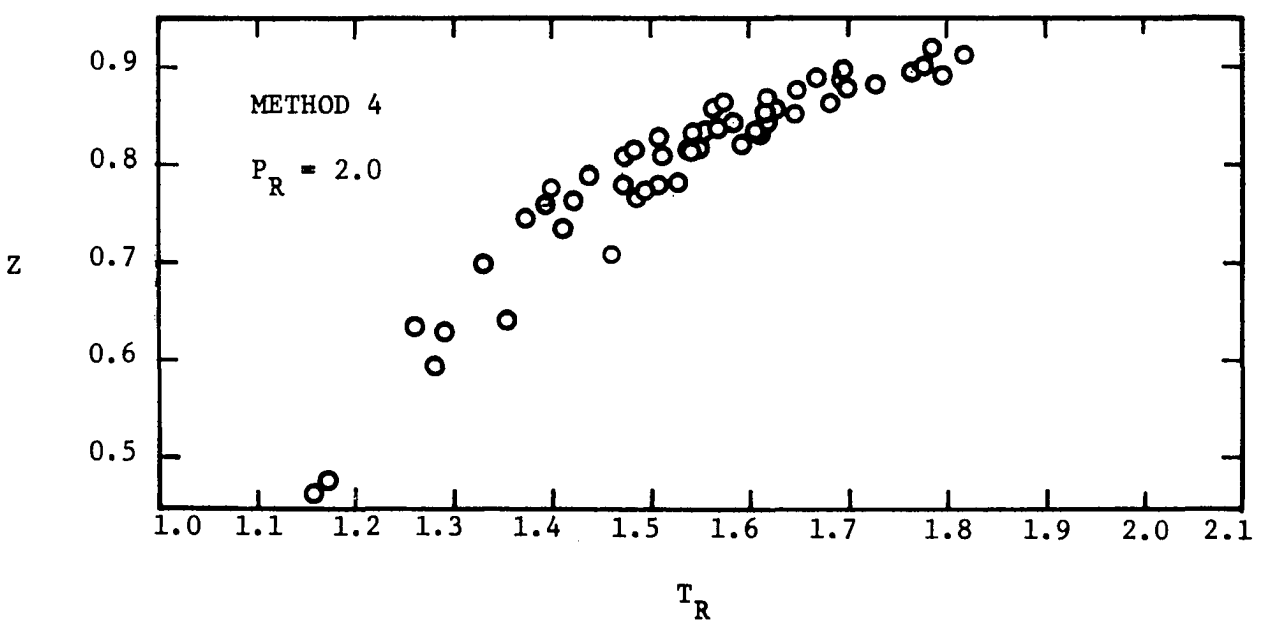


FIGURE 7-11. COMPRESSIBILITY FACTOR VERSUS REDUCED TEMPERATURE AT P_R = 2.0.

CHAPTER VIII

CONSTRUCTION OF GENERALIZED LIQUID DENSITY CHART

It has been found that a linear relationship exists between the Eykman dimensionless refractive index function and density, for the normal hydrocarbons and their mixtures in the liquid state (see Figure 8-1).

At this point it is to be recalled that the constancy of the Eykman Molecular Refraction equation at elevated temperatures and pressures and in both the gaseous and liquid phases have been established. Utilizing density data from the API Project 44, the Eykman dimensionless refractive index function and refractive indicies were calculated at elevated temperatures by means of the following relationships.

Let
$$(n^2-1)/(n+0.4) = \xi_E \tag{8-1}$$

then,
$$\xi_E = (EMR)\ \rho/MW \tag{8-2}$$

but
$$EMR = 2.185 + 0.7357\ MW \tag{6-4}$$

$$\xi_E = \rho[(2.185/MW) + 0.7357] \tag{8-3}$$

Equation (8-1) can be written as:

$$n^2 - n\xi_E - 0.4 \quad \xi_E - 1 = 0 \tag{8-4}$$

Solving for n by means of the simple quadratic equation we have:

$$n = \frac{\xi_E \pm \sqrt{(\xi_E)^2 + 1.6\ \xi_E + 4.0}}{2.0} \tag{8-5}$$

Values for normal heptane to normal dodecane can be found tabulated in Appendix K1.

Figure 8-2 is a plot of the Eykman dimensionless refractive index function versus temperature in degrees centigrade for various liquid hydrocarbons and their mixtures. The lines of constant EMR (or MW) will each develop some curvature and approach a value of approximately 0.177 at their respective critical point -- since $n_c \simeq 1.127$.

Next the data of Doolittle (25) for densities of normal liquid hydrocarbons at elevated temperatures and pressures were used to construct a generalized density chart (see Figure 8-3). A sample calculation is given in Appendix K2. Additional isotherms in Figure 8-3 may be constructed in a similar manner to that outlined.

A. Procedure for the Application of the Proposed Method

Find the density of a pure liquid paraffin hydrocarbon component at some elevated temperature and pressure.

1. If the pure component is unknown identify by using any of the following figures: 6-3, 6-4, 6-5, 6-6, 8-1 or 8-2.
2. If the pure component is known, then T_R, P_R, EMR and MW are known.

3. From Figure 8-2 evaluate ξ_E.

4. From Figure 8-3 obtain ρ/ξ_E.

5. Solve for ρ at the required temperature and pressure.

Find the density of an unknown normal hydrocarbon liquid mixture at some elevated temperature and pressure.

1. Measure the density at atmospheric conditions.

2. Obtain EMR from Figure 6-4.

3. Get reduced temperature and pressure from either Figures 7-1 and 7-2, or Figures 7-7 or 7-8.

4. From Figure 8-2 obtain $(n^2-1)/(n^2+0.4)$ by interpolating between the EMR or MW values of the pertinent pure compounds.

5. Enter Figure 8-4 and compute the value of ρ at the required conditions.

A sample calculation is given in Appendix K2.

Using pure hydrocarbon data the curves in Figures 7-1, 7-2, 7-7 and 7-8 can be extended. With the appropriate data, additional isotherms may be constructed in Figure 8-3.

B. Summary

Current liquid density correlations for pure components or mixtures will allow no better than a crude approximation. In the majority of cases these methods utilize the corresponding states concept and as such use a reference density to evaluate a reduced density. The reference density is for the most part the critical density; a property not easily obtained for pure components and obtained with considerably less assurance for their mixtures.

The fact is that any generalized liquid density correlation that utilizes a constant density datum in order to obtain reduced densities will inevitably result in erroneous numerical values for density. What is needed is a "Variable datum", which would make allowances for intermolecular behavior and changes in structure. The Eykman dimensionless refractive index ratio, ξ_E, is such a datum.

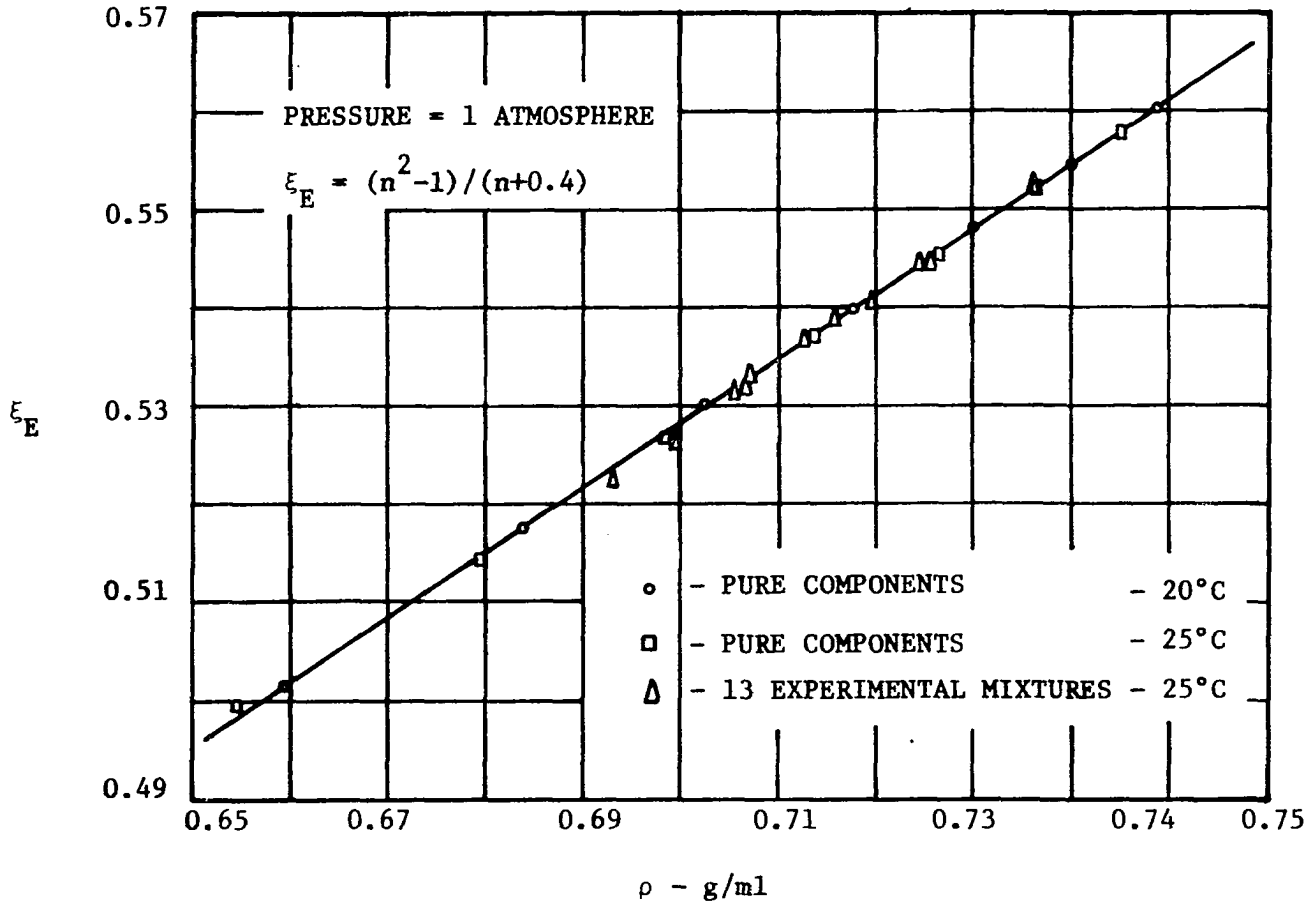


FIGURE 8-1. EYKMAN DIMENSIONLESS REFRACTIVE INDEX FUNCTION VERSUS DENSITY (g/ml)

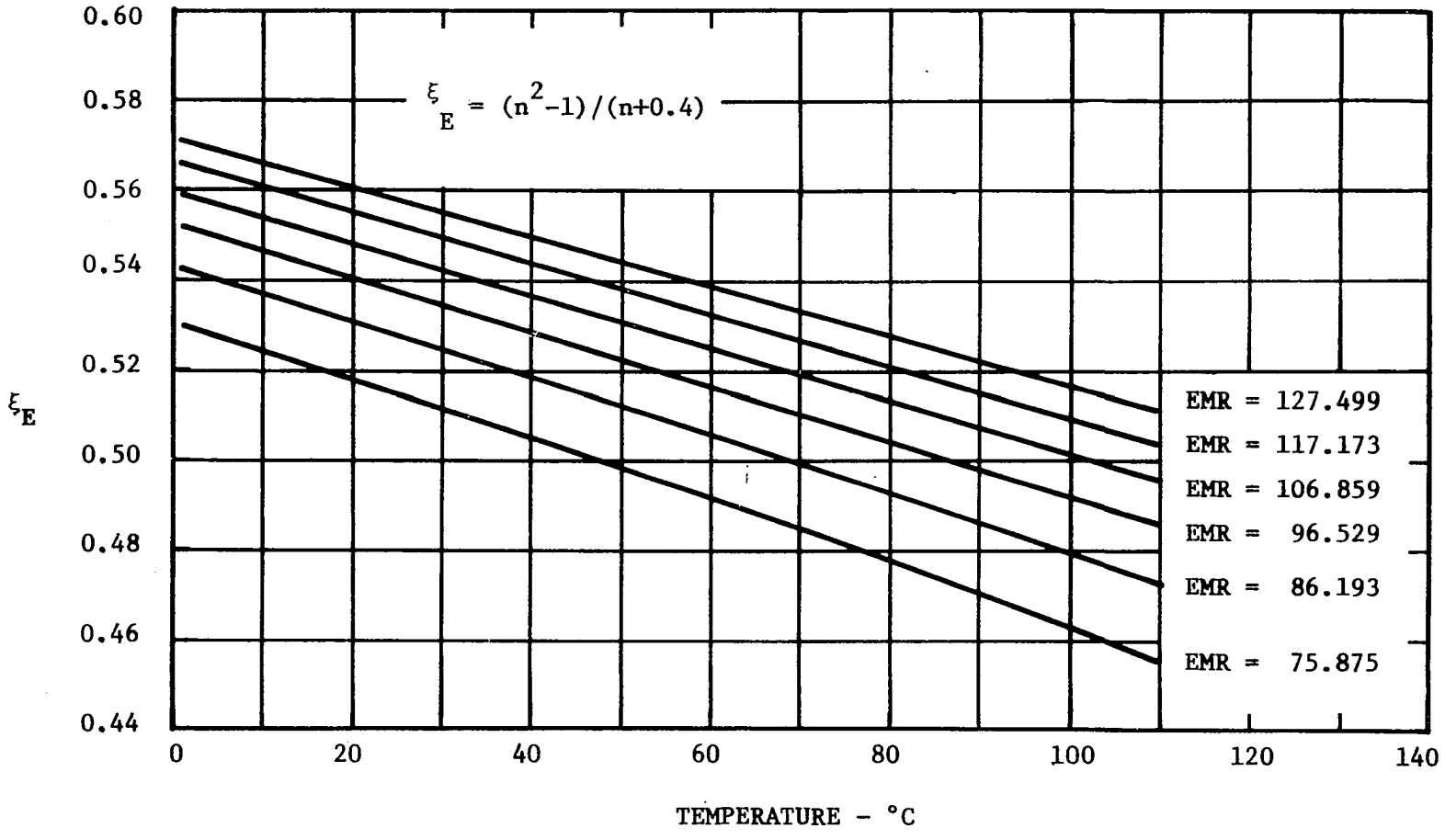


FIGURE 8-2. EYKMAN DIMENSIONLESS REFRACTIVE INDEX FUNCTION VERSUS TEMPERATURE (°C)

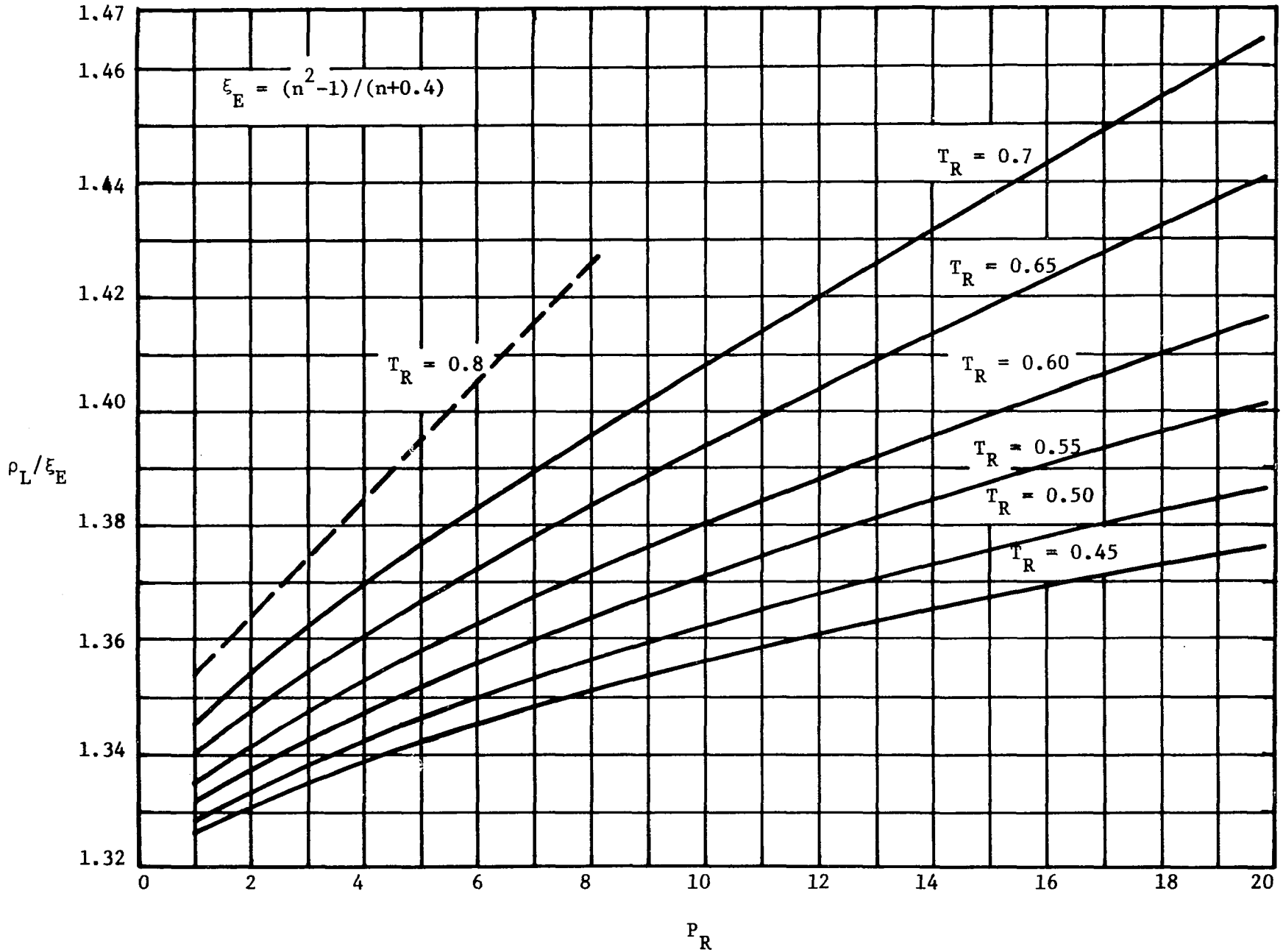


FIGURE 8-3. GENERALIZED LIQUID DENSITY CHART

CHAPTER IX

POTENTIAL APPLICATIONS FOR EYKMAN MOLECULAR REFRACTION

This study has also revealed that EMR is a good correlating parameter for liquid viscosities of pure hydrocarbons and their mixtures at atmospheric pressure and different temperatures. The correlation takes the form of a family of straight lines on a semi-log plot as seen in Figure 9-1, and can be mathematically written as:

$$\mu_L = 10^{[a+b(EMR)]} \qquad (9-1)$$

where a and b are temperature-dependent constants of the given series. Similar curves can be drawn for other homologous series.

Moreover, there have been published several generalized correlations of viscosity based on the concept of corresponding states. All these approaches use a reference viscosity in order to evaluate reduced viscosities. The reference used is either the critical viscosity or the viscosity at the temperature in question but at atmospheric pressure. Since the viscosity of a fluid mixture at the critical point is generally unknown or easily estimated, this approach becomes highly questionable. The correlations utilizing the ratio of the viscosity to its value at the same temperature but at atmospheric pressure as a

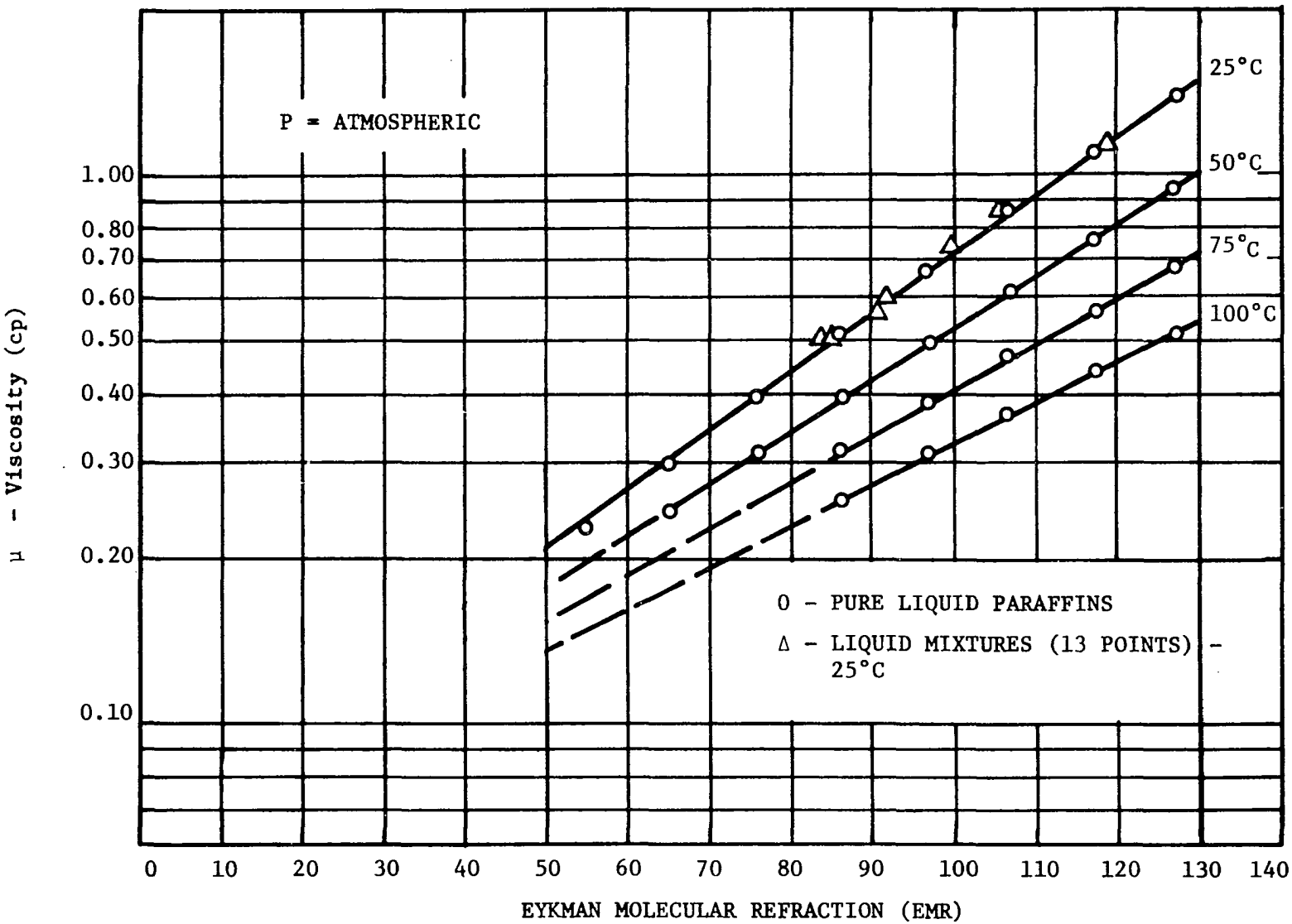


FIGURE 9-1. VISCOSITY VERSUS EYKMAN MOLECULAR REFRACTION (EMR)

function of reduced temperatures and pressures, have, on occasions, given acceptable results. Nevertheless, there is a great deal of room for improvement. The author believes that a more reliable generalized viscosity curve (for gases and liquids) utilizing the dimensionless Eykman refractive index function, could be constructed as was done in the case of the proposed generalized liquid density curve. Therefore, it is recommended that available viscosity data at elevated temperatures and pressures be utilized for this purpose.

Examination of the physical properties of the pure hydrocarbons would reveal that there is an orderly behavior between the Eykman Molecular Refraction formula and surface tension, latent heats of vaporization, thermal conductivity, heat capacity, and sonic velocity. Therefore it is reasonable to assume that similar correlations could exist between EMR and the mixture of the compounds in question.

The results of this work, along with the suggested ideas, could provide a good foundation for future studies of the interrelationship of the Eykman Molecular Refraction formula and the behavior of hydrocarbon mixtures.

CHAPTER X

CONCLUSIONS

An improved equation of state has been developed for complex gas mixtures containing both high molecular weight non polar gases, heptanes plus, and one or more polar compounds.

The improved equation of state makes use of Eykman Molecular Refraction (EMR) as a third parameter and can be functionally represented thus:

$$Z = \phi\ (P_R, T_R, EMR)$$

This form of the equation of state has the following advantages over those now in use.

1. The accuracy of the graphical solution of the equation, the generalized Z chart number 1, is far superior to any of the other compressibility charts in existence.
2. The proposed mixing rule technique, whereby the components of a given hydrocarbon mixture (containing other compounds) are split into two groups - H_2S, N_2, CO_2, nC_1 and nC_2^+ - is simpler and more reliable than any current two constant pseudo critical approach whether based on the

semi-empirical equations of state or the Lennard-Jones Potential Function.

3. The proposed third parameter, EMR, is an easily measurable characterization parameter for the heptanes plus.
4. The value of EMR varies over a wide range. From 13.984 for Methane (MW = 16.042) to 127.499 for Dodecane (MW = 170.328) making accurate interpolation possible.
5. This characteristic parameter, EMR, recognizes both intermolecular forces and molecular structure.

The linear relationship between EMR and molecular weight for pure components as well as their mixtures (in a given homogenous series), the constancy of EMR with change in temperature and pressure, and the fact that all substances have approximately the same refractive index at the critical point, have led to choice of this property as a characterization parameter in this improved equation of state.

A new generalized liquid density chart was also proposed. This chart is potentially better than current charts in that this correlation utilizes a "variable" datum to evaluate density at new temperatures and pressures. The remarkable thing about this variable datum is the fact that it makes allowances not only for intermolecular behavior, as other approaches do, but it also makes allowances for changes in structure.

BIBLIOGRAPHY

1. Abbiss, C. P., Knobler, C. M., Teague, R. K., and Pings, C. J. "Refractive Index and Lorentz-Lorenz Function for Saturated Argon, Methane, and Carbon Tetrafluoride," Jour. of Chem. Physics (June 15, 1965) 42, No. 12, 4145-4148.

2. American Petroleum Institute. Selected Values of Properties of Hydrocarbons. Research Project 44 at National Bureau of Standards (1949).

3. American Petroleum Institute (Division of Refining). Bibliography of Volumetric and Thermodynamic Data for Pure Hydrocarbons and Their Mixtures (1964) Bibliography No. 3.

4. Beale, E. S. L., in Science of Petroleum. (Ed. by Dunstan, A. E. et al.) London: Oxford University Press (1938) 2, 1136.

5. Bicher, Leo B., and Katz, Donald L. "Viscosities of the Methane-Propane System," Ind. Eng. Chem. (1943) 35, No. 7, 754.

6. Bicher, L. B., and Katz, D. L. "Viscosity of Natural Gases," Trans. AIME (1944) 155, 246.

7. Bottchen, C. J. F. "The Dependence Upon Pressure of the Molecular Polarization of Dipole-Free Gases and Liquids," Physica (1942) 9, 945-953.

8. Bromley, L. A., and Wilke, C. R. "Viscosity Behavior of Gases," Ind. Eng. Chem. (1951) 43, No. 7, 1641.

9. Brown, G. G., et al. Natural Gasoline and the Volatile Hydrocarbons. NGAA, Tulsa, Oklahoma (1948).

10. Buron W. Proc. Roy. Soc. (1908) 132, 395-405.

11. Buxton, T. S. The Prediction of the Compressibility Factor for Lean Natural Gas-Carbon Dioxide Mixtures at High Pressure. Ph. D. Thesis, University of Oklahoma (1965).

12. Carr, Norman L., Kobayashi, Riki, and Burrows, David B. "Viscosity of Hydrocarbon Gases Under Pressure," Pet. Trans, AIME (1954) T.P. 3915, 201.

13. Carr, N. L., Parent, J. D., and Peck, R. E. "The Viscosity of Gases and Gas Mixtures at High Pressures," paper presented at the AIChE Regional Mtg. in San Francisco (Sept. 13-16, 1953).

14. Chang, Z. T. Chinese J. Phys. 1 (1934) 1.

15. Comings, E. W., and Egly, R. S. "Viscosity of Gases and Vapors at High Pressures," Ind. Eng. Chem. (1940) 32, No. 5, 714-18.

16. Comings, E. W., Mayland, B. J., and Egly, R. S. "The Viscosity of Gases at High Pressure," University of Illinois Engineering Experiment Station Bulletin No. 354 (1944), 42.

17. Corner, J. Proc. Camb. Phil. Soc. (1946) 42, 328-337.

18. Cuthbertson, C., and Cuthbertson, M. Proc. Roy. Soc. (1909) 133, 166-176.

19. Cuthbertson, C., and Cuthbertson, M. "The Refraction and Dispersion of Neon and Helium," Proc. Roy. Soc. (London), Series A (1932) 135, 40-47.

20. Cuthbertson, C., and Cuthbertson, M. "On the Refraction and Dispersion of Air, Oxygen, Nitrogen, and Hydrogen, and Their Relations," Proc. Roy. Soc. (London), Series A (1910) 83, 151-176.

21. Cuthbertson, C., and Cuthbertson, M. "On the Refraction and Dispersion of Carbon Dioxide, Carbon Monoxide, and Methane," Proc. Roy. Soc. (London), Series A (1920) 97, 152-159.

22. Danforth, W. E. Phys. Rev. (1931) 38, 1224.

23. Debye, P. Polar Molecules. Dover Publishing Co. (1929) 36-37.

24. Dodge, B. F. Chemical Engineering Thermodynamics. New York: McGraw-Hill Book Co., Inc. (1944).

25. Doolittle, A. K. "Specific Volumes of n-Alkanes," J. of Chem. & Eng. Data (1964) 9, No. 2, 275.

26. Dreisbach, R. R. "Applicability of the Eykman Equation," Ind. Eng. Chem. (1948) 12, 2269-2271.

27. Edgar, G., and Calingaert, G. J. Am. Chem. Soc. (1929) 51, 1940.

28. Edminster, W. C. Applied Hydrocarbon Thermodynamics. Houston: Gulf Publishing Co. (1961).

29. Egloff, G. Physical Constants of Hydrocarbons. New York: Reinhold Publishing Company. Vol. I (1939); Vol. II (1940); Vol. III (1946); Vol. IV (1947).

30. Eykman, J. F. Rec. trav. chim. (1895) 14, 185.

31. Eyring, H., Hildebrand, J., and Rice, S. "The Liquid State," International Science & Tech. (March, 1963) 56.

32. Fajans, K., and Kreidl, N. J. J. Amer. Ceram. Soc. (1948) 31, 105.

33. Fox, G. W., and Ryan, A. H. "The Dielectric Constants of Ammonia, Nitrogen, and Carbon Dioxide at Ultra-High Frequency," Physical Review (1939) 56, 1132-1136.

34. Freibug, S. Z. Physik. (1927) 41, 378.

35. Gibson, R. E., and Kincaid, J. F. J. Am. Chem. Soc. (1938) 60, 511.

36. Gilman, H. Organic Chemistry. New York: John Wiley & Sons, Inc. (1943) 1741.

37. Glasstone, S. Textbook of Physical Chemistry. New York: D. Van Nostrand Co. (1940).

38. Grosse, A. V., and Woekher, R. C. Ind. Eng. Chem. Anal. Ed. (1941) 11, 614.

39. Guggenheim, E. A. Mixtures. Oxford: Clarendon Press (1952) 156-65.

40. Hanson, G. H., Kuist, B. B., and Brown, G. G. "Liquid Densities of Volatile Hydrocarbon Mixtures," I.&E.C. (December, 1944) 36, 1161.

41. Herning, F., and Zipperer, L. "Calculation of the Viscosity of Technical Gas Mixtures from the Viscosity of the Individual Gases," Gas and Wasserfoch (1936) 79, 49.

42. Hill, T. L. Statistical Mechanics. New York: McGraw-Hill Book Co., Inc. (1956).

43. Hirshfelder, J. O. A Generalized Equation of State for Both Gases and Liquids. A report prepared by Naval Research Laboratory, Dept. of Chemistry, University of Wisconsin, Madison, Wisconsin (Oct. 5, 1956) Wis-OOR-15, Ser. 10.

44. Hirshfelder, J. O., Curtiss, C. F., and Bird, R. B. Molecular Theory of Gases and Liquids. New York: John Wiley & Sons, Inc. (1954).

45. Hirschfelder, J. O., et al. J. Chem. Phys. (1948) 16, 968-81.

46. Hirschfelder, J. O., et al. J. Chem. Phys. (1948) 44, 205-31.

47. Hirschfelder, J. O., et al. "Viscosity and Other Properties of Gases and Gas Mixtures," Trans. AIME (1949) 71, 921.

48. Holmes, J. J. Sci. Inst. (1945) 22, 219.

49. Hougen, O. A., Watson, K. M., and Ragatz, R. A. Chemical Process Principles, Part II. New York: John Wiley & Sons, Inc. (1959).

50. Jeans, Sir J. An Introduction to the Kinetic Theory of Gases. New York: Macmillan Company (1940).

51. Jenkins, H. O. "Effect of Pressure on the Refractive Indices in Gases," Trans. Faraday Soc. (1934) 30, 752.

52. Joffe, J. Chem. Eng. Prog. (1949) 45, 160.

53. Joffe, J. Ind. Eng. Chem. (1947) 39, No. 7, 837.

54. Johnston, G. I., et al. "Dielectric Constants of Imperfect Gases. Helium, Argon, Nitrogen and Methane," J. Chem. Phys. (1960) 33, No. 5, 1310.

55. Kay, W. B. "Density of Hydrocarbon Gases and Vapors," Ind. Eng. Chem. (1936) 28, 1014.

56. Kay, W. B. J. Am. Chem. Soc. (1946) 68, 1336.

57. Katz, D. L., et al. Handbook of Natural Gas Engineering. New York: McGraw-Hill Book Co., Inc. (1959).

58. Keyes, F. G., and Kirkwood, J. G. "The Dielectric Constant of Carbon Dioxide as a Function of Temperature and Density," Physical Review (1930) 36, 754-761.

59. Kirkwood, J. G. "The Theory of Dielectric Polarization," J. of Chem. Phys. (1936) 4, 592-601.

60. Kurata, F., and Katz, D. L. Trans. Am. Inst. Chem. Engrs. (1942) 38, 995.

61. Kurtz, S. S., Jr., and Headington, C. E. Ind. Eng. Chem. Anal. Ed. (1937) 9, 21.

62. Kurtz, S. S., Jr., and Lipkin, M. R. J. Am. Chem. Soc. (1941) 63, 2158.

63. Kurtz, S. S., Jr., and Ward, A. L. J. Franklin Inst. (1936), 222, 563.

64. Kurtz, S. S., Jr., and Ward, A. L. J. Franklin Inst. (1937) 224, 583, 697.

65. Larsen, T. Z. Physik. (1933) 111, 394.

66. Leland, T. W., Jr., Koboyaski, Riki, and Mueller, William H. "Application of the Corresponding States Principle to Mixtures of Low Molecular Weight Gases at Low Temperatures and High Pressures," A.I.Ch.E. (December, 1961) 7, No. 4, 535.

67. Leland, T. W., and Mueller, W. H. "Applying the Theory of Corresponding States to Multicomponent Systems," Ind. Eng. Chem. (1959) 41, 597.

68. Lennard-Jones, J. E. "On the Determination of Molecular Fields-II from the Equation of State of a Gas," Proc. Roy. Soc. (London), A106 (1924) 463.

69. Lewis, G. N., and Randall, M. Thermodynamics. New York: McGraw-Hill Book Co., Inc. (1961).

70. Lipkin, M. R., and Kurtz, S. S., Jr. Ind. Eng. Chem. Anal. Ed. (1941) 13, 291.

71. Lowery, H. Proc. Phys. Soc. (London) (1927) 39, 421.

72. Lowery, H. "I. The Refraction and Dispersion of (1), Air, (2) Oxygen, (3) Gaseous Chloroform; II. New Determination of the Gaseous Refractivities of (1) Acetone, (2) Methyl Ether, (3) Ethyl Ether," Proc. Phys. Soc. (London) (1927) 40, 23-28.

73. Lyderson, A. L., Greenkorn, R. A., and Hougen, O. A. Generalized Thermodynamic Properties of Pure Fluids. Engineering Experiment Station Report No. 4, Madison, Wisconsin: University of Wisconsin (1955).

74. Mathias, H. S. J. Am. Chem. Soc. (1950) 72, 1897.

75. Meissner, H. P., and Seferian, R. "PVT Relations of Gases," Chem. Eng. Prog. (1951) 47, 579-84.

76. Meissner, H. P. "Critical Constants from Parachor and Molar Refraction," Chem. Eng. Prog. (1949) 45, 149-153.

77. Mibashan, A. Trans. Faraday Soc. (1945) 41, 374.

78. Michels, A., de Boer, and Bijl, A. "Molecular Interaction and Its Influence on the Polarizability," Physica (1937) 4, 981-994.

79. Michels, A., and Hamers, J. "The Effect of Pressure on the Refractive Index of Carbon Dioxide," Physics (1937) 4, 995-1006.

80. Michels, A., and Kleerekoper, L. "Measurements of Dielectric Constant of Carbon Dioxide at 25, 50, and 100° up to 1700 Atmospheres," Physica (1939) 6, 586-590.

81. Moelwyn-Hughes, E. A. Physical Chemistry. New York: Pergamon Press (1961).

82. Nelson, L. C., and Obert, E. F. "Generalized PVT Properties of Gases," Trans. ASME (October, 1954) 1057-66.

83. Oleson, F. B., and Bennett, C. E. "Molecular Refraction of Carbon Dioxide as a Function of Density," Physical Review (1941) 60, 171.

84. Phillips, P. "The Relation Between the Refractivity and Density of Carbon Dioxide," Proc. Roy. Soc. (London), Series A (1920) 97, 225-240.

85. Pitzer, K. S. J. Am. Chem. Soc. (1955) 77, 3427.

86. Pitzer, K. S. J. Chem. Phys. (1939) 7, 583.

87. Prigogine, I. Advances in Chemical Physics. Vol. 1. New York: Interscience Publishing Co. (1958).

88. Ramaswamy, K. L. "Dielectric Polarization and the Structure of the Carbon Dioxide Molecule," Proc. Indian Academy of Science (1937) A6, 301-311.

89. Rankine, A. O. "On a Method of Determining the Viscosity of Gases," Proc. Roy. Soc. (1910) 83A, 265.

90. Reamer, H. H., et al. Ind. Eng. Chem. (1944) 36, 956.

91. Reamer, H. H., Sage, B. H., and Lacey, W. W. "Phase Equilibria in Hydrocarbon Systems-C_1nC_4-nC_{10} System," Ind. and Eng. Chem. (1947) 39, 77.

92. Reamer, H. H., Sage, B. H., and Lacey, W. W. Ind. & Eng. Chem. (1950) 42, 534.

93. Reid, R. C., and Sherwood, T. K. The Properties of Gases and Liquids. New York: McGraw-Hill Book Co., Inc. (1958).

94. Rosebush, W. H., and Eddy, C. R. J. Chem. Physics (1940) 8, 424.

95. Rossini, F. D. J. Research, Nat'l Bureau of Standards (1934) 13,21.

96. Rossini, F. D. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds. Pittsburgh, Pa.: Carnegie Press (1953).

97. Rowlinson, J. S. Liquid and Liquid Mixtures. London: Butterworth Science Publishing Co. (1959).

98. Sage, B. H., and Lacey, W. N. "Effect of Pressure Upon Viscosity of Methane and Two Natural Gases," Trans. AIME (1938) 127, 118.

99. Sage, B. H., et al. Ind. Eng. Chem. (1937) 29, 658.

100. Sage, B. H., and Lacey, W. N. Ind. Eng. Chem. (1939) 31, 1947.

101. Sage, B. H., and Lacey, W. N. Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide, and Carbon Dioxide. New York: API (1955).

102. Sage, B. H., and Lacey, W. N. Thermodynamic Properties of Lighter Paraffins, Hydrocarbons and Nitrogen. New York: API (1950).

103. Sage, B. H., and Lacey, W. N. Volumetric and Phase Behavior of Hydrocarbons. Houston, Texas: Gulf Publishing Co. (1949).

104. Sarem, A. M. Investigation of the Densities of Coexisting Liquid and Vapor for Light Hydrocarbons their Mixtures Near the Critical Region. Ph.D. Thesis, University of Oklahoma, Norman, Oklahoma (1964).

105. Satter, Abdus. Nonideal Behavior of Gases and their Mixtures. Ph.D. Thesis, University of Oklahoma, Norman, Oklahoma (1963).

106. Shepard, A. F., Henne, A. L., and Midgley, T., Jr. J. Am. Chem. Soc. (1931) 53, 1948.

107. Smiles, S. "The Relation Between Chemical Constitution and Physical Properties," Longmans, Green, London (1910).

108. Smith, C. P. Dielectric Behavior and Structure. New York: McGraw-Hill Book Co., Inc. (1955).

109. Smith, C. Proc. Roy. Soc. (A) 87, 366-71.

110. Smith, A. S., and Brown, G. G. "Correlating Fluid Viscosity," Ind. Eng. Chem. (1943) 35, 705.

111. Smyth, C. P., Engel, E. W., and Wilson, E. Bright. J. Am. Chem. Soc. (1929) 51, 1736.

112. Smyth, C. P., and Stoops, W. N. J. Am. Chem. Soc. (1928) 50, 1883.

113. Smyth, C. P. Dielectric Constant and Molecular Structure. New York: Chemical Catalog Co. (1931).

114. Standing, M. B., and Katz, D. L. "Density of Crude Oils Saturated with Natural Gas," Trans. AIME (1949) 146, 159.

115. Standing, M., and Katz, D. L. Trans. AIME (1942) 146, 140.

116. Stewart, W. F., Burkhardt, S. F., and Voo, D. Prediction of Pseudocritical Parameters for Mixtures. Presented at the A.I.Ch.E. Mtg., Kansas City, Mo. (1959).

117. Stockmeyer, W. H. "Second Virial Coefficient of Polar Gases," J. Chem. Pys. (1941) 9398.

118. Swietoslawski, W. J. Am. Chem. Soc. (1920) 42, 1945.

119. Uhlig, H. H., Kirkwood, J. G., and Keyes, F. G. J. Chem. Phys. (1933) 1, 155.

120. Uyehara, O. A., and Watson, K. M. "A Universal Viscosity Correlation," National Petroleum News (October 4, 1944) R 714.

121. Uyehara, O. A., and Watson, K. M. National Petroleum News (1944), R 764.

122. van der Waals, J. D., Sr. Die Kontinuitate des gasformigen un flussigen Zustandes. Doctoral Dissertation, University of Leiden (1873).

123. van Itterbeck, A., and Spaepen, J. "Measurements of the Dielectric Constant of Gaseous CO_2 to Ten Atmospheres," Physica (1944) 11, 43-48.

124. van Itterbeck, A., and Spaepen, J. "Measurements on the Dielectric Constants of Several Non-polar Gases (H, D. He, 0 and Air) and CO Between 20° K, and Ordinary Temperatures," Physica (1943) 10, 173-184.

125. van Vleck, J. H. "The Theory of Electric and Magnetic Susceptibilities," London: Oxford Press (1932), 15, 16 and 54.

126. Walsh, J. L., Ahlgerg, J. H., and Nilson, E. N. J. of Math. & Mech. (1962) 11, No. 2.

127. Wan, S. W. "Determination of Critical Temperatures from Index of Refraction," (1941) 45, 903-907.

128. Ward, A. L., and Fulweiler, W. H. Ind. Eng. Chem. (1934) 6.

129. Ward, A. L., and Kurtz, S. S., Jr. Ind. Eng. Chem. Anal. Ed. (1938) 10, 559.

130. Watson, K. M. "Thermodynamics of the Liquid State, Generalized Predictions of Properties," I.&E.C. (April, 1943), 398.

131. Watson, H. E., and Ramaswamy, K. L. Proc. Roy. Soc. (London) (1936) A-156, 144.

132. Watson, H. E., Rao, G. G., and Ramaswamy, K. L. "The Dielectric Coefficients of Gases - Part I. The Rare Gases and Hydrogen," Proc. Roy. Soc. (London) Series A (1932) 132, 569-585.

133. Watson, H. E., Rao, G. G., and Ramaswamy, K. L. "The Dielectric Coefficient of Gases - Part II. The Lower Hydrides of Carbons and Silicon, Oxygen, Nitrogen, Oxides of Nitrogen and Carbon, and Fluorides of Silicon and Sulphur," Proc. Roy. Soc. (London) Series A (1934) A143, 558-588.

134. Watson, K. M., and Smith, R. L. National Pet. News (July, 1936).

135. Weinaug, C. F., and Katz, D. L. Ind. Eng. Chem. (1943) 35, 239.

136. Zahn, C. T., and Miles, J. B., Jr. "The Dielectric Constant and the Electric Moment of CO, COS, CS_2, and H_2S," Physical Review (1928) 32, 497-504.

137. Phillips Petroleum Company; Private Communication.

APPENDIX A

NOMENCLATURE

TABLE A1

NOMENCLATURE

a	= van der Waal intermolecular force correction constant
a'	= Constant in Dieterici's equation of state
a''	= Constant in Berthelot's equation of state
$\bar{a}$	= Any constant in the semi-empirical equations of state
b	= van der Waal volume correction constant
b'	= Constant in Dieterici's equation of state
b''	= Constant in Berthelot's equation of state
$B(T)$	= Second virial coefficient of the virial equation expressed in the form of power series in specific volume
$B'(T)$	= Second virial coefficient of the virial equation expressed in the form of power series in pressure
c	= Constant in equations of state of pure gases
c'	= Constant in equations of state of gas mixtures
C	= Constant in equation (4-14)
$C(T)$	= Third virial coefficient of the virial equation expressed in the form of power series in specific volume
$C'(T)$	= Third virial coefficient of the virial equation expressed in the form of power series in pressure
$D(T)$	= Fourth virial coefficient of the virial equation expressed in the form of power series in specific volume
$D'(T)$	= Fourth virial coefficient of the virial equation expressed in the form of power series in pressure
e	= Exponential
F	= Dimensionless molecular parameter as defined in equation (7-2)
$^\circ F$	= Degree Fahrenheit
f	= Functional notation

f' = First derivative of function

h = Plank's constant

i = Subscript denoting ith component or molecule

j = Subscript denoting jth component or molecule

$^{\circ}K$ = Degree Kelvin

k = Boltzmann's constant

kT = Energy per molecule

L = Length of a molecule

MW = Molecular weight

m = Mass of a molecule

$\hat{N}$ = Number of molecules in a system

N = Avogadro's number

$\hat{n}$ = Number of components in a system

n = Refractive index

n_c = Critical refractive index

n_g = Number of moles of gas

P = Absolute pressure

P_a = Sugden's parachor

P_c = Critical pressure

P_c^* = Pseudocritical pressure

P_s = Saturation pressure

P_r = Reduced pressure

R = Universal gas constant

R_D = Lorentz-Lorenz molecular refraction measured by the D-line of sodium

$^{\circ}R$ = Degree Rankine

r = Distance between two molecules

T = Absolute thermodynamic temperature

T_R = Reduced temperature

T_c = Critical temperature

T_c^* = Pseudocritical temperature

U(r) = Intermolecular potential function

V = Total volume of a system

v = Molar volume ($v = V/n_g$)

V = Specific molar volume of a component at the pressure and temperature of a mixture

V_c = Critical volume

V_R = Reduced volume

W = Absolute weight of a molecule

X = Mole fraction of a component in a mixture

X^* = "Pseudo" mole fraction of a component in a mixture

Z = Compressibility factor

Z° = Compressibility factor of an ideal substance with zero acentric factor

Z^1 = Slope of the compressibility factor vs acentric factor curve at a given reduced temperature and pressure

Z_c = Critical compressibility factor

expt = Experimental

EMR = Eykman Molecular Refraction

mix = Mixture

EMRI = Eykman Molecular Refractivity Intercept

α = A function of temperature and pressure

$\gamma(\rho)$ = A density function

$\bar{\gamma}$ = Surface tension

$\hat{\epsilon}$ = Magnitude of the potential energy minimum

ε = Dielectric constant

ρ_c = Critical density

ρ_g = Density of vapor

ρ_L = Density of liquid

σ = Collision diameter of low velocity collision betw-en two molecules

ϕ = Functional notation

ω = Acentric factor

ω' = Pseudoacentric factor of a mixture

Π_E = Electronic polarization measured by the D-line of sodium

α_E = Electronic polarizability

ξ = Dimensionless ratio (Lorentz-Lorenz)

ξ = Dimensionless ratio (Eykman)

μ = Viscosity

μ_L = Liquid viscosity

χ = Reciprocal of Satter's dimensionless parameter F

APPENDIX B

PHYSICAL CONSTANTS

TABLE B1

PHYSICAL CONSTANTS

Compound	Molecular Weight	Critical Temperature °R	Critical Pressure Psia
nC_1	16.042	343.30	673.10
nC_2	30.068	549.77	708.30
nC_3	44.094	665.95	617.40
nC_4	58.120	765.31	550.70
iso-C_4	58.120	734.65	529.10
nC_5	72.146	845.60	489.50
iso-C_5	72.146	829.80	483.00
nC_6	86.172	914.20	439.70
iso-C_6	86.172	896.60	440.14
nC_7	100.198	972.31	396.90
nC_8	114.224	1024.31	362.10
nC_9	128.250	1073.00	345.00
nC_{10}	142.276	1114.70	306.00
nC_{11}	156.302	1153.70	282.00
nC_{12}	170.378	1187.70	263.00
N_2	28.016	227.20	492.00
CO_2	44.010	548.00	1073.00
H_2S	34.076	672.70	1306.00
O_2	32.000	278.00	730.00

APPENDIX C

THIRD PARAMETERS

TABLE C1

EYKMAN MOLECULAR REFRACTION (EMR), Z_c AND ω DATA

Simple Almost Spherical Non-Polar Molecules			
Compound	Eykman Molecular Refraction	Z_c	ω
H_e	1.117	0.300	-
N_e	2.136	0.307	-
H_2	4.365	0.304	-0.3540
A	8.837	0.291	-0.0020
X_e	21.828	0.293	0.0020
N_2	9.407	0.292	0.0350
O_2	8.495	0.292	-0.0169
CO_2	15.750	0.275	0.2250
nC_1	13.984	0.290	0.0130

TABLE C1 -- Continued

Compound	Eykman Molecular Refraction	Z_c	ω
Hydrocarbons			
nC_2	23.913	0.288	0.0150
nC_3	34.316	0.278	0.1520
nC_4	44.243	0.274	0.2010
iso-C_4	44.741	0.283	0.1918
nC_5	55.267	0.268	0.2520
iso-C_5	55.302	0.269	0.2060
nC_6	65.575	0.264	0.2899
iso-C_6	-	-	0.2824
nC_7	75.875	0.260	0.3520
nC_8	86.193	0.256	0.3992
nC_9	96.529	0.250	0.4439
nC_{10}	106.859	0.246	0.4869
nC_{11}	117.173	0.243	0.5009
nC_{12}	127.499	0.237	0.5394
Polar Molecules			
H_2S	19.828	0.284	0.1060

APPENDIX D

EYKMAN MOLECULAR REFRACTION

NORMAL HYDROCARBONS

(nC_1-nC_{12})

PURE COMPONENTS AT 25°C AND 20°C

TABLE D1

PURE COMPONENTS

Temperature = 25°C

Component	Molecular Weight	ρ (density)	n (refractive index)	$\frac{n^2-1}{n+0.4}$	$\frac{n^2-1}{n+0.4}\frac{1}{\rho}$	$\frac{n^2-1}{n+0.4}\frac{M}{\rho}$ = EMR
Methane	16.042					13.984
Ethane	30.068					23.913
Propane	44.094	0.4928				34.316
Butane	58.120	0.5730	1.32920	0.44342	0.77385	44.9767
Pentane	72.146	0.6214	1.35472	0.47602	0.76604	55.2667
Hexane	86.172	0.6548	1.37226	0.49829	0.76098	65.5752
Heptane	100.198	0.6795	1.38511	0.51455	0.75725	75.8749
Octane	114.224	0.6985	1.39505	0.52709	0.75460	86.1934
Nonane	128.250	0.7138	1.40311	0.53725	0.75266	96.5286
Decane	142.276	0.7263	1.40967	0.54550	0.75107	106.8592
Undecane	156.302	0.7366	1.41500	0.55220	0.74966	117.1733
Dodecane	170.328	0.7452	1.41949	0.55782	0.74855	127.4990

TABLE D1 -- Continued

Temperature = 20°C

Component	Molecular Weight	ρ (density)	n (refractive index)	$\frac{n^2-1}{n+0.4}$	$\frac{n^2-1}{n+0.4}\frac{1}{\rho}$	$\frac{n^2-1}{n+0.4}\frac{M}{\rho}$ = EMR
Methane	16.042					
Ethane	30.068					
Propane	44.094	0.5005				
Butane	58.120	0.5788	1.33260	0.44778	0.77363	44.9634
Pentane	72.146	0.6262	1.35748	0.47952	0.76576	55.2465
Hexane	86.172	0.6594	1.37486	0.50158	0.76066	65.5476
Heptane	100.198	0.6838	1.38765	0.51775	0.75716	75.8659
Octane	114.224	0.7025	1.39743	0.53009	0.75488	86.1911
Nonane	128.250	0.7176	1.40542	0.54016	0.75273	96.5376
Decane	142.276	0.7300	1.41189	0.54828	0.75107	106.8592
Undecane	156.302	0.7402	1.41716	0.55490	0.74966	117.1733
Dodecane	170.328	0.7487	1.42160	0.56047	0.74859	127.5058
Iso-Butane						44.741

APPENDIX E

EYKMAN MOLECULAR REFRACTION

NORMAL HYDROCARBON MIXTURES

(nC_7-nC_{12})

(a) MIXTURE COMPOSITION

(b) EXPERIMENTAL RESULTS

TABLE E1

COMPOSITION OF EXPERIMENTAL LIQUID MIXTURES

Components	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5
nC_7	0.5508	0.4748	0.4319	0.5555	
nC_8	0.3038	0.3496			0.4922
nC_9			0.2900	0.2619	0.5078
nC_{10}	0.1454	0.1756	0.2781		
nC_{11}					
nC_{12}				0.1826	

	Mixture 6	Mixture 7	Mixture 8	Mixture 9	Mixture 10
nC_7	0.5325				
nC_8		0.4868	0.5666	0.3446	
nC_9		0.1915		0.3086	0.5645
nC_{10}	0.1810				
nC_{11}		0.3217	0.4334	0.3468	0.4355
nC_{12}	0.2865				

TABLE E1 -- Continued

Components	Mixture 11	Mixture 12	Mixture 13
nC_7			
nC_8			
nC_9	0.5529	0.5417	
nC_{10}			0.2241
nC_{11}	0.4471	0.4583	0.4501
nC_{12}			0.3258

TABLE E2

EXPERIMENTAL RESULTS - MIXTURES

Temperature - 25°C

Sample No.	Molecular Weight	ρ (density)	n (refractive index)	$\frac{n^2-1}{n+0.4}$	$\frac{n^2-1}{n+0.4}\frac{1}{\rho}$	$\frac{n^2-1}{n+0.4}\frac{M}{\rho}$ = EMR
1	110.578	0.6930	1.39271	0.5241	0.7563	83.6301
2	112.495	0.6955	1.39404	0.5258	0.7560	85.0462
3	120.042	0.7054	1.39862	0.5316	0.7536	90.4636
4	120.346	0.7064	1.39874	0.5317	0.7527	90.5844
5	121.346	0.7069	1.39958	0.5328	0.7537	91.4585
6	127.906	0.7127	1.40281	0.5369	0.7533	96.3516
7	130.449	0.7155	1.40436	0.5388	0.7530	98.2281
8	132.462	0.7174	1.40537	0.5401	0.7529	99.7306
9	133.145	0.7198	1.40566	0.5405	0.7510	99.9919
10	140.468	0.7247	1.40898	0.5446	0.7515	105.5617
11	140.791	0.7255	1.40898	0.5446	0.7507	105.6918
12	141.105	0.7259	1.40918	0.5449	0.7507	105.9275
13	157.729	0.7363	1.41551	0.5528	0.7508	118.4229

APPENDIX F

COMPRESSIBILITY CHART DATA

COMPOSITION OF MIXTURES

TABLE F1

COMPOSITION DATA FOR GAS COMPRESSIBILITY CHART

Mixture 1

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
N_2	0.0046	492.00	227.20	0.2920
CO_2	0.0050	1073.00	548.00	0.2750
H_2S	0.2260	1306.00	672.70	0.2840
C_1	0.7561	673.10	343.30	0.2900
C_2	0.0071	708.30	549.77	0.2880
C_3	0.0008	617.40	665.95	0.2780
iC_4	0.0002	529.10	734.65	0.2830
nC_4	0.0002	550.10	765.31	0.2770

TABLE F1 -- Continued

Mixture 2

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
N_2	0.0046	492.00	227.20	0.2920
CO_2	0.0030	1073.00	548.00	0.2750
H_2S	0.1438	1306.00	672.70	0.2840
C_1	0.8414	673.10	343.30	0.2900
C_2	0.0059	708.30	549.77	0.2880
C_3	0.0008	617.40	665.95	0.2780
iC_4	0.0003	529.10	734.65	0.2830
nC_4	0.0002	550.70	765.31	0.2770

TABLE F1 -- Continued

Mixture 3

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
N_2	0.0052	492.00	227.20	0.2920
CO_2	0.0131	1073.00	548.00	0.2750
H_2S	0.0570	1306.00	672.70	0.2840
C_1	0.9151	673.10	343.30	0.2900
C_2	0.0084	708.30	549.77	0.2880
C_3	0.0008	617.40	665.95	0.2780
iC_4	0.0002	529.10	734.65	0.2830
nC_4	0.0002	550.70	765.31	0.2770

TABLE F1 -- Continued

Mixture 4

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.8977	673.10	343.30	0.2900
C_2	0.0464	708.30	549.77	0.2880
N_2	0.0053	492.00	227.20	0.2920
CO_2	0.0506	1073.00	548.00	0.2750

TABLE F1 -- Continued

Mixture 5

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.8520	673.10	343.30	0.2900
C_2	0.0410	708.30	549.77	0.2880
N_2	0.0057	492.00	227.20	0.2920
CO_2	0.1013	1073.00	548.00	0.2750

TABLE F1 -- Continued

Mixture 6

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.7458	673.10	343.30	0.2900
C_2	0.0474	708.30	549.77	0.2880
N_2	0.0052	492.00	227.20	0.2920
CO_2	0.2016	1073.00	548.00	0.2750

TABLE F1 -- Continued

Mixture 7

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.7593	673.10	343.30	0.2900
C_3	0.1316	617.40	665.95	0.2780
CO_2	0.1091	1073.00	548.00	0.2750

TABLE F1 -- Continued

Mixture 8

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.5841	673.10	343.30	0.2900
C_2	0.2867	708.30	549.77	0.2880
CO_2	0.1292	1073.00	548.00	0.2750

TABLE F1 -- Continued

Mixture 9

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.8710	673.10	343.30	0.2900
C_2	0.0640	708.30	549.77	0.2880
H_2S	0.0650	1306.00	672.70	0.2840

TABLE F1 -- Continued

Mixture 10

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.8310	673.10	343.30	0.2900
C_2	0.0710	708.30	549.77	0.2880
H_2S	0.0980	1306.00	672.70	0.2840

TABLE F1 -- Continued

Mixture 11

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.8360	673.10	343.30	0.2900
C_2	0.1170	708.30	549.77	0.2880
H_2S	0.0470	1306.00	672.70	0.2840

TABLE F1 -- Continued

Mixture 12

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.8000	673.10	343.30	0.2900
C_2	0.1070	708.30	549.77	0.2880
H_2S	0.0930	1306.00	672.70	0.2840

TABLE F1 -- Continued

Mixture 13

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.7130	673.10	343.30	0.2900
C_2	0.0900	708.30	549.77	0.2880
H_2S	0.1970	1306.00	672.70	0.2840

TABLE F1 -- Continued

Mixture 14

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.9388	673.10	343.30	0.2900
C_2	0.0395	708.30	549.77	0.2880
C_3	0.0122	617.40	665.95	0.2780
iC_4	0.0091	529.10	734.65	0.2830
C_5S	0.0030	486.25	837.70	0.2685
C_6S	0.0010	439.92	905.35	0.2640

TABLE F1 -- Continued

Mixture 15

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.9080	673.10	343.30	0.2900
C_2	0.0423	708.30	549.77	0.2880
C_3	0.0198	617.40	665.95	0.2780
iC_4	0.0138	529.10	734.65	0.2830
C_5S	0.0063	486.25	837.70	0.2685
C_6S	0.0043	439.92	905.35	0.2640
C_7+	0.0055	396.90	972.31	0.2600

TABLE F1 -- Continued

Mixture 16

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
N_2	0.0750	492.00	227.20	0.2920
C_1	0.6007	673.10	343.30	0.2900
C_2	0.1477	708.30	549.77	0.2880
C_3	0.1342	617.40	665.95	0.2780
iC_4	0.0144	529.10	734.65	0.2830
nC_4	0.0237	550.70	765.31	0.2770
C_5S	0.0043	486.25	837.70	0.2685

TABLE F1 -- Continued

Mixture 17

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
N_2	0.0375	492.00	227.20	0.2920
C_1	0.5904	673.10	343.30	0.2900
C_2	0.2037	708.30	549.77	0.2880
C_3	0.1403	617.40	665.95	0.2780
iC_4	0.0081	529.10	734.65	0.2830
nC_4	0.0176	550.70	765.31	0.2770
C_5S	0.0024	486.25	837.70	0.2685

TABLE F1 -- Continued

Mixture 18

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.6742	673.10	343.30	0.2900
C_2	0.1675	708.30	549.77	0.2880
C_3	0.1584	617.40	665.95	0.2780

TABLE F1 -- Continued

Mixture 19

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
N_2	0.0584	492.00	227.20	0.2920
C_1	0.5435	673.10	343.30	0.2900
C_2	0.1632	708.30	549.77	0.2880
C_3	0.1620	617.40	665.95	0.2780
iC_4	0.0587	529.10	734.65	0.2830
C_5S	0.0091	486.25	837.70	0.2685
C_6S	0.0018	439.92	905.35	0.2640

TABLE F1 -- Continued

Mixture 20

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.9148	673.10	343.30	0.2900
C_2	0.0371	708.30	549.77	0.2880
C_3	0.0247	617.40	665.95	0.2780
iC_4	0.0208	529.10	734.65	0.2830
C_5S	0.0026	486.25	837.70	0.2685

TABLE F1 -- Continued

Mixture 21

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.8984	673.10	343.30	0.2900
C_2	0.0507	708.30	549.77	0.2880
C_3	0.0251	617.40	665.95	0.2780
iC_4	0.0176	529.10	734.65	0.2830
C_5S	0.0062	486.25	837.70	0.2685
C_6S	0.0014	439.92	905.35	0.2640
C_7+	0.0008	396.90	972.31	0.2600

TABLE F1 -- Continued

Mixture 22

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
N_2	0.0081	492.00	227.20	0.2920
CO_2	0.0180	1073.00	548.00	0.2750
C_1	0.8499	673.10	343.30	0.2900
C_2	0.0664	708.30	549.77	0.2880
C_3	0.0267	617.40	665.95	0.2780
iC_4	0.0107	529.10	734.65	0.2830
nC_4	0.0091	550.70	765.31	0.2770
iC_5	0.0082	829.80	483.00	0.2690
C_6S	0.0019	439.92	905.35	0.2640
C_7+	0.0010	396.90	972.31	0.2600

TABLE F1 -- Continued

Mixture 23

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
C_1	0.9463	673.10	343.30	0.2900
C_2	0.0254	708.30	549.77	0.2880
C_3	0.0146	617.40	665.95	0.2780
iC_4	0.0046	529.10	734.65	0.2830
nC_4	0.0038	550.70	765.31	0.2770
iC_5	0.0036	829.80	483.00	0.2690
C_6S	0.0017	439.92	905.35	0.2640

TABLE F1 -- Continued

Mixture 24

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
CO_2	0.0061	1073.00	548.00	0.2750
C_1	0.8500	673.10	343.30	0.2900
C_2	0.0600	708.30	549.77	0.2880
C_3	0.0332	617.40	665.95	0.2780
iC_4	0.0085	529.10	734.65	0.2830
nC_4	0.0129	550.70	765.31	0.2770
nC_5	0.0066	829.80	483.00	0.2690
C_6S	0.0109	439.92	905.35	0.2640
C_7+	0.0062	396.90	972.31	0.2600

TABLE F1 -- Continued

Mixture 25

Component	Mol Fraction	Critical Pressure (Psia)	Critical Temperature (°R)	Critical Compressibility Factor
CO_2	0.0040	1073.00	548.00	0.2750
C_1	0.9432	673.10	343.30	0.2900
C_2	0.0390	708.30	549.77	0.2880
C_3	0.0117	617.40	665.95	0.2780
iC_4	0.0008	529.10	734.65	0.2830
nC_4	0.0013	550.70	765.31	0.2770

APPENDIX G

COMPRESSIBILITY CHART DATA

EXPERIMENTAL COMPRESSIBILITY FACTORS

TABLE G1

EXPERIMENTAL COMPRESSIBILITY FACTORS

Mixture 1

Pressure Psia	Z		
	40°F	100°F	175°F
600	0.8470	0.8946	0.9325
1000	0.7476	0.8380	0.9000
1500	0.6390	0.7785	0.8654
2000	0.5877	0.7305	0.8394
2500	0.5950	0.7131	0.8260
3000	0.6321	0.7221	0.8250
4000	0.7320	0.7833	0.8560
5000	0.8451	0.8700	0.9138

TABLE G1 -- Continued

Mixture 2

Pressure Psia	Z				
	40°F	65°F	100°F	135°F	175°F
625.5	0.8658				
847.6	0.8199				
1022.1	0.7868				
1521.3	0.7058				
2021.0	0.6616				
2520.8	0.6626				
3020.8	0.6903				
4020.7	0.7810				
5020.6	0.8874				
2021.0	0.6617				
623.9		0.8887			
822.8		0.8585			
1022.2		0.8278			
1521.4		0.7630			
2021.4		0.7222			
2521.6		0.7156			
3021.8		0.7320			
4022.0		0.8068			
5022.1		0.9025			
3021.9		0.7320			
607.3			0.9106		
624.7			0.9088		
823.5			0.8863		
1022.7			0.8638		
1521.7			0.8152		
2021.2			0.7828		
2521.0			0.7731		
3020.8			0.7813		
3520.7			0.8046		
4020.7			0.8374		
4520.6			0.8761		
5020.6			0.9191		
3020.8			0.7809		
654.8				0.9256	
823.7				0.9106	
1022.9				0.8937	
1521.8				0.8582	
2021.3				0.8338	
2521.0				0.8255	

TABLE G1 -- Continued

Pressure Psia	Z				
	40°F	65°F	100°F	135°F	175°F
3020.9				0.8299	
4020.9				0.8734	
5020.5				0.9412	
564.8					0.9459
823.3					0.9295
1022.6					0.9183
1521.7					0.8911
2021.2					0.8736
2521.0					0.8668
3020.8					0.8694
4020.6					0.9026
5020.5					0.9579
3020.8					0.8687

TABLE G1 -- Continued

Mixture 3				Mixture 4			
	Z				Z		
Pressure Psia	60°F	100°F	175°F	Pressure Psia	100°F	130°F	160°F
600	0.8920	0.9125	0.9505	1026	0.8805	0.9044	0.9246
1000	0.8194	0.8826	0.9290	1526	0.8437	0.8752	0.8993
1500	0.7510	0.8426	0.9088	2026	0.8183	0.8547	0.8847
2000	0.7106	0.8161	0.8960	2526	0.8108	0.8508	0.8793
2500	0.7074	0.8075	0.8915	3026	0.8223	0.8574	0.8845
3000	0.7304	0.8145	0.8970	3526	0.8455	0.8771	0.9007
4000	0.8144	0.8674	0.9320	4026	0.8778	0.9041	0.9225
5000	0.9180	0.9450	0.9860	4526	0.9166	0.9373	0.9537
				5026	0.9591	0.9741	0.9881
				6026	1.0502	1.0562	1.0640
				7026	1.1456	1.1430	1.1428

TABLE G1 -- Continued

Pressure Psia	Mixture 5 Z			Mixture 6 Z		
	100°F	130°F	160°F	100°F	130°F	160°F
1026	0.8813	0.9040	0.9234	0.8652	0.8887	0.9095
1526	0.8378	0.8715	0.8987	0.8141	0.8519	0.8818
2026	0.8117	0.8501	0.8824	0.7783	0.8251	0.8600
2526	0.8043	0.8443	0.8766	0.7676	0.8136	0.8499
3026	0.8148	0.8509	0.8825	0.7783	0.8196	0.8549
3526	0.8377	0.8697	0.8985	0.8037	0.8393	0.8704
4026	0.8708	0.8968	0.9210	0.8380	0.8669	0.8933
4526	0.9096	0.9304	0.9492	0.8787	0.9022	0.9239
5026	0.9520	0.9688	0.9832	0.9231	0.9408	0.9562
6026	1.0445	1.0516	1.0583	1.0178	1.0261	1.0339
7026	1.1397	1.1392	1.1385	1.1156	1.1158	1.1154

TABLE G1 -- Continued

Pressure Psia	Mixture 7 Z			Mixture 8 Z		
	100°F	130°F	160°F	100°F	130°F	160°F
1026	0.8128	0.8509	0.8739	0.8128	0.8509	0.8739
1526	0.7500	0.7985	0.8344	0.7500	0.7985	0.8344
2026	0.7142	0.7703	0.8101	0.7142	0.7703	0.8101
2526	0.7140	0.7633	0.8037	0.7140	0.7633	0.8037
3026	0.7369	0.7779	0.8134	0.7369	0.7779	0.8134
3526	0.7754	0.8080	0.8361	0.7754	0.8080	0.8361
4026	0.8206	0.8454	0.8665	0.8206	0.8454	0.8665
4526	0.8707	0.8892	0.9030	0.8707	0.8892	0.9030
5026	0.9226	0.9361	0.9449	0.9226	0.9361	0.9449
6026	1.0312	1.0350	1.0359	1.0312	1.0350	1.0359
7026	1.1408	1.1361	1.1279	1.1408	1.1361	1.1279

TABLE G1 -- Continued

Pressure Psia	Mixture 9 Z 101.5°F	Mixture 9 Z 130.9°F	Mixture 9 Z 160°F	Mixture 10 Z 101.8°F	Mixture 10 Z 131.7°F	Mixture 10 Z 161.1°F
1026	0.886	0.907	0.920	0.872	0.897	0.915
2026	0.811	0.852	0.883	0.790	0.833	0.863
3026	0.813	0.861	0.880	0.791	0.827	0.860
4026	0.869	0.898	0.918	0.851	0.874	0.898
5026	0.951	0.989	0.982	0.937	0.947	0.961
6026	1.044	1.053	1.056	1.032	1.032	1.037
7026	1.141	1.141	1.138	1.130	1.122	1.120

TABLE G1 -- Continued

Pressure Psia	Mixture 11 Z			Mixture 12 Z		
	101.0°F	129.7°F	160.2°F	101.7°F	130.6°F	160.3°F
1026	0.865	0.887	0.911	0.851	0.874	0.896
2026	0.785	0.825	0.861	0.761	0.804	0.840
3026	0.789	0.826	0.859	0.766	0.803	0.837
4026	0.853	0.876	0.900	0.833	0.855	0.880
5026	0.942	0.954	0.967	0.923	0.934	0.948
6026	1.039	1.042	1.047	1.022	1.023	1.029
7026	1.141	1.134	1.131	1.124	1.116	1.113

TABLE G1 -- Continued

Mixture 13

Pressure Psia	Z		
	101.8°F	130.5°F	161.0°F
1026	0.830	0.856	0.880
2026	0.714	0.762	0.807
3026	0.717	0.754	0.794
4026	0.786	0.808	0.835
5026	0.882	0.889	0.905
6026	0.982	0.979	0.985
7026	1.085	1.072	1.071

TABLE G1 -- Continued

Mixture 14		Mixture 15		
Pressure Psia	Z 80°F	Pressure Psia	Z 80°F	Z 40°F
500	0.935	500	0.921	
1000	0.874	1000	0.843	
1500	0.822	1500	0.776	
2000	0.790	2000	0.738	
		2500	0.741	
		3000	0.763	
		3500	0.798	0.757
		4000	0.847	
		4500	0.898	
		5000	0.946	
		5500	0.998	
		6000	1.051	

TABLE G1 -- Continued

Pressure Psia	Mixture 16 Z			Mixture 17 Z		
	20°F	80°F	140°F	20°F	80°F	140°F
500	0.737	0.845	0.904	0.641	0.803	0.880
1000	0.559	0.700	0.813	0.477	0.638	0.753
1500	0.438	0.603	0.741			0.651
2000	0.489	0.586	0.707			0.631
2500	0.566	0.620	0.715			0.657
3000	0.645	0.677	0.745			0.706
3500	0.723	0.738	0.788			0.762
4000	0.802	0.803	0.837			0.825
4500	0.882	0.869	0.892			0.888
5000	0.962	0.934	0.949			0.957
5500		1.000	1.007			

TABLE G1 -- Continued

Pressure Psia	Mixture 18 Z 80°F	Mixture 18 Z 140°F	Mixture 19 Z 30°F	Mixture 19 Z 80°F	Mixture 19 Z 140°F
500	0.850	0.906	0.710	0.822	0.889
1000	0.704	0.818	0.532	0.651	0.774
1500	0.600	0.743	0.423	0.537	0.688
2000	0.578	0.708	0.476	0.543	0.660
2500	0.616	0.714	0.557	0.598	0.679
3000	0.670	0.743	0.650	0.668	0.723
3500	0.732	0.784	0.722	0.738	0.774
4000	0.794	0.834	0.803	0.808	0.832
4500	0.862	0.889	0.886	0.880	0.893
5000	0.928	0.941	0.968	0.951	0.958
5500		1.011			

TABLE G1 -- Continued

Pressure Psia	Mixture 20 Z 60°F	Mixture 20 Z 100°F	Mixture 21 Z 60°F	Mixture 21 Z 100°F
500	0.909	0.931	0.901	0.923
1000	0.820	0.864	0.805	0.852
1500	0.750	0.809	0.734	0.797
2000	0.712	0.784	0.696	0.767
2500	0.712	0.783	0.697	0.763
3000	0.740	0.799	0.728	0.779
3500	0.780	0.828	0.771	0.806
4000	0.828	0.864	0.818	0.844
4500	0.881	0.908	0.870	0.887
5000	0.937	0.951	0.924	0.932
5500	0.991	0.997	0.976	0.981

TABLE G1 -- Continued

Pressure Psia	Mixture 22 Z 200°F	113.4°F	88.3°F	Mixture 23 Z 150°F	110°F	85°F
500	0.960	0.925	0.902	0.954	0.940	0.929
1000	0.927	0.862	0.823	0.913	0.889	0.869
1500	0.900	0.811	0.756	0.879	0.845	0.819
2000	0.884	0.775	0.725	0.867	0.823	0.789
2500	0.882	0.772	0.728	0.870	0.822	0.787
3000	0.891	0.797	0.755	0.881	0.834	0.802
3500	0.910	0.821	0.787	0.898	0.854	0.827

TABLE G1 -- Continued

	Mixture 24			Mixture 25		
	Z					
	199.7°F	152.4°F	81°F	150°F	110°F	90.6°F
500	0.960	0.947	0.918	0.958	0.939	0.929
1000	0.929	0.903	0.842	0.925	0.895	0.875
1500	0.906	0.868	0.777			
2000	0.892	0.848	0.742			
2500	0.890	0.843	0.739			
3000	0.889	0.853	0.765			
3500	0.916	0.877	0.802			

APPENDIX H

SUMMARY OF EXAMINED

COMBINATION RULES

COMPARISON OF PSEUDO-CRITICAL METHODS

TABLE H1

SUMMARY OF OTHER COMBINATION RULES

EXAMINED

Virial Approach Intermediate Between van der Waal's and Berthelot Equations:

$$\frac{T_{c_{mix}}}{P_{c_{mix}}} = \sum_{i=1}^{n} = x_i \frac{T_{c_i}}{P_{c_i}}$$

$$\frac{\left(T_{c_{mix}}\right)^{5/4}}{\left(P_{c_{mix}}\right)^{1/2}} = \sum_{i=1}^{n} = x_i \frac{T_{c_i}^{5/4}}{P_{c_i}^{1/2}}$$

Virial Approach Based on Berthelot Equation:

$$\frac{T_{c_{mix}}}{P_{c_{mix}}} = \frac{1}{3} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_i}} \right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}} \right)^{1/3} \right]^3$$

$$\frac{T_{c_{mix}}^3}{P_{c_{mix}}} = \frac{1}{8} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_j}} \right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}} \right)^{1/3} \right]^3 T_{c_i} T_{c_j}$$

Virial Approach. Extension of Joffe's Preferred Method:

$$\frac{T_{c_{mix}}}{P_{c_{mix}}} = \frac{1}{8} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_i}} \right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}} \right)^{1/3} \right]^3$$

$$\frac{T_{c_{mix}}}{P_{c_{mix}}^{1/2}} = \sum_{i=1}^{n} x_i \frac{T_{c_i}}{P_{c_i}^{1/2}}$$

Kay's Rule (see Page 13).

Leland and Mueller (see Page 16).

Virial Approach of Stewart, Burkhardt and Voo:

$$J = \frac{T_{c_{mix}}}{P_{c_{mix}}} = \frac{1}{3} \sum_{i=1}^{n} x_i \frac{T_{c_i}}{P_{c_i}} + \frac{2}{3} \left[\sum_{i=1}^{n} x_i \left(\frac{T_{c_i}}{P_{c_i}} \right)^{1/2} \right]^2$$

$$K = \frac{T_{c_{mix}}}{\left(P_{c_{mix}} \right)^{1/2}} = \sum_{i=1}^{n} x_i \frac{T_{c_i}}{P_{c_i}^{1/2}}$$

$$T_{c_{mix}} = K^2/J$$

$$P_{c_{mix}} = T_{c_{mix}}/J$$

Empirical Statistical Mechanical Approach:

$$T_{c_{mix}} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[(T_{c_{ii}})(T_{c_{jj}}) \right]^{1/2}$$

$$T_{c_{mix}} = \sum_{i=1}^{n} x_i Z_{c_i}$$

$$P_{c_{mix}} = \frac{}{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3}$$

TABLE H2

COMPARISON OF PSEUDO-CRITICAL METHODS

Mixture 1		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	799.05	410.28
Van der Waal-Berthelot (Intermediate Virial)	809.06	415.57
Berthelot (Virial)	819.68	420.85
Kay	817.45	420.12
Leland and Mueller	808.47	415.83
Joffe	799.19	410.58
Stewart, Burkhardt and Voo	800.26	410.85
This Study:		
Method I	789.52	404.79
Method II	819.43	420.12
Method III	303.95	296.85
Method IV	770.84	430.83

TABLE H2 -- Continued

Mixture 2		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	751.53	385.40
Van der Waal-Berthelot (Intermediate Virial)	758.77	389.24
Berthelot (Virial)	766.62	393.11
Kay	764.57	392.42
Leland and Mueller	749.09	384.80
Joffe	751.62	385.66
Stewart, Burkhardt and Voo	752.62	385.66
This Study:		
Method I	751.20	384.92
Method II	765.85	392.42
Method III	404.90	311.78
Method IV	782.88	405.88

TABLE H2 -- Continued

Mixture 3		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	707.33	362.79
Van der Waal-Berthelot (Intermediate Virial)	711.23	364.94
Berthelot (Virial)	715.62	367.03
Kay	713.67	366.30
Leland and Mueller	705.35	362.40
Joffe	707.49	363.07
Stewart, Burkhardt and Voo	708.43	363.31
This Study:		
Method I	712.79	365.66
Method II	714.04	366.30
Method III	729.99	364.58
Method IV	811.90	381.14

TABLE H2 -- Continued

Mixture 4		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	691.31	360.43
Van der Waal-Berthelot (Intermediate Virial)	694.97	362.88
Berthelot (Virial)	699.58	364.73
Kay	694.00	362.62
Leland and Mueller	691.36	361.08
Joffe	693.51	361.78
Stewart, Burkhardt and Voo	694.40	362.01
This Study:		
Method I	726.47	370.79
Method II	710.46	362.62
Method III	772.84	375.11
Method IV	707.64	362.20

TABLE H2 -- Continued

Mixture 5		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	709.19	368.82
Van der Waal-Berthelot (Intermediate Virial)	713.31	371.44
Berthelot (Virial)	718.48	373.63
Kay	714.02	371.83
Leland and Mueller	708.33	369.00
Joffe	710.92	369.92
Stewart, Burkhardt and Voo	711.85	370.16
This Study:		
Method I	729.15	372.16
Method II	728.51	371.83
Method III	805.45	386.20
Method IV	718.22	369.07

TABLE H2 -- Continued

Mixture 6		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	745.87	389.17
Van der Waal-Berthelot (Intermediate Virial)	751.19	392.52
Berthelot (Virial)	758.21	395.57
Kay	754.44	393.75
Leland and Mueller	744.24	388.98
Joffe	747,63	390.28
Stewart, Burkhardt and Voo	748.59	390.53
This Study:		
Method I	746.83	381.55
Method II	770.70	393.75
Method III	902.58	415.79
Method IV	763.77	389.01

TABLE H2 -- Continued

Mixture 7		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	696.28	400.74
Van der Waal-Berthelot (Intermediate Virial)	705.13	412.45
Berthelot (Virial)	733.52	423.19
Kay	709.39	408.09
Leland and Mueller	710.27	409.44
Joffe	711.78	410.84
Stewart, Burkhardt and Voo	712.50	411.05
This Study:		
Method I	887.82	460.96
Method II	786.00	408.09
Method III	574.15	381.28
Method IV	680.05	408.09

TABLE H2 -- Continued

Mixture 8		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	725.97	423.09
Van der Waal-Berthelot (Intermediate Virial)	734.53	430.75
Berthelot (Virial)	749.52	436.60
Kay	734.85	428.94
Leland and Mueller	733.05	427.90
Joffe	735.82	428.94
Stewart, Burkhardt and Voo	736.59	429.16
This Study:		
Method I	977.39	488.30
Method II	858.57	428.94
Method III	683.43	418.19
Method IV	727.77	428.94

TABLE H2 -- Continued

Mixture 9		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	709.53	373.44
Van der Waal-Berthelot (Intermediate Virial)	715.48	377.34
Berthelot (Virial)	723.19	380.62
Kay	716.49	377.92
Leland and Mueller	710.48	374.57
Joffe	712.54	375.23
Stewart, Burkhardt and Voo	713.45	375.47
This Study:		...
Method I	762.17	389.77
Method II	738.99	377.92
Method III	812.92	388.46
Method IV	815.31	388.49

TABLE H2 -- Continued

Mixture 10		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	727.51	384.30
Van der Waal-Berthelot (Intermediate Virial)	734.65	388.94
Berthelot (Virial)	744.09	393.05
Kay	737.62	390.24
Leland and Mueller	728.42	385.42
Joffe	730.67	386.19
Stewart, Burkhardt and Voo	731.60	386.43
This Study:		
Method I	781.05	399.97
Method II	762.04	390.24
Method III	871.10	403.81
Method IV	857.34	401.34

TABLE H2 -- Continued

Mixture 11		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	701.37	378.38
Van der Waal-Berthelot (Intermediate Virial)	708.50	383.59
Berthelot (Virial)	718.31	387.55
Kay	706.96	382.93
Leland and Mueller	705.10	381.02
Joffe	707.03	381.67
Stewart, Burkhardt and Voo	707.89	381.90
This Study:		
Method I	787.63	404.92
Method II	744.86	382.93
Method III	741.31	385.76
Method IV	799.34	397.66

TABLE H2 -- Continued

Mixture 12		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	725.60	389.81
Van der Waal-Berthelot (Intermediate Virial)	733.45	395.31
Berthelot (Virial)	744.53	399.99
Kay	735.72	396.02
Leland and Mueller	728.16	391.84
Joffe	730.37	392.60
Stewart, Burkhardt and Voo	731.27	392.84
This Study:		
Method I	800.62	411.76
Method II	770.02	396.02
Method III	880.32	412.43
Method IV	851.65	407.10

TABLE H2 -- Continued

Mixture 13		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	782.35	417.40
Van der Waal-Berthelot (Intermediate Virial)	791.74	423.56
Berthelot (Virial)	805.25	429.60
Kay	800.94	426.77
Leland and Mueller	782.71	418.29
Joffe	785.50	419.30
Stewart, Burkhardt and Voo	785.50	419.30
This Study:		
Method I	835.67	429.95
Method II	829.48	426.77
Method III	491.92	359.89
Method IV	816.13	440.78

TABLE H2 -- Continued

Mixture 14		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	670.58	360.96
Van der Waal-Berthelot (Intermediate Virial)	671.97	364.54
Berthelot (Virial)	681.82	368.66
Kay	674.12	362.23
Leland and Mueller	672.07	362.36
Joffe	670.94	362.97
Stewart, Burkhardt and Voo	673.35	363.62
This Study:		
Method I	705.81	360.17
Method II	709.84	362.23
Method III	378.31	298.71
Method IV	609.00	361.46

TABLE H2 -- Continued

Mixture 15		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	658.52	368.01
Van der Waal-Berthelot (Intermediate Virial)	664.17	378.33
Berthelot (Virial)	695.56	389.85
Kay	667.79	372.81
Leland and Mueller	673.16	376.80
Joffe	673.55	377.70
Stewart, Burkhardt and Voo	674.21	377.89
This Study:		
Method I	751.67	384.78
Method II	728.29	372.81
Method III	462.05	333.14
Method IV	622.36	375.38

TABLE H2 -- Continued

Mixture 16		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	642.99	414.41
Van der Waal-Berthelot (Intermediate Virial)	660.13	436.17
Berthelot (Virial)	699.57	452.58
Kay	651.46	426.15
Leland and Mueller	670.49	432.78
Joffe	670.75	434.08
Stewart, Burkhardt and Voo	671.23	434.24
This Study:		
Method I	1014.75	545.53
Method II	792.69	426.15
Method III	572.37	426.60
Method IV	666.80	453.58

TABLE H2 -- Continued

Mixture 17		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	654.51	427.54
Van der Waal-Berthelot (Intermediate Virial)	669.63	447.12
Berthelot (Virial)	704.34	461.62
Kay	661.89	438.05
Leland and Mueller	678.98	444.18
Joffe	679.35	445.40
Stewart, Burkhardt and Voo	679.84	445.56
This Study:		
Method I	941.73	534.06
Method II	772.44	438.05
Method III	349.26	356.51
Method IV	592.66	440.60

TABLE H2 -- Continued

Mixture 18		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	664.50	420.53
Van der Waal-Berthelot (Intermediate Virial)	677.55	436.83
Berthelot (Virial)	707.01	448.79
Kay	670.24	429.02
Leland and Mueller	685.06	434.20
Joffe	685.53	435.33
Stewart, Burkhardt and Voo	686.14	435.52
This Study:		
Method I	931.38	516.08
Method II	774.26	429.02
Method III	518.54	395.80
Method IV	638.34	430.22

TABLE H2 -- Continued

Mixture 19		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	634.41	435.39
Van der Waal-Berthelot (Intermediate Virial)	653.43	461.63
Berthelot (Virial)	701.21	481.64
Kay	646.45	449.83
Leland and Mueller	669.06	459.82
Joffe	671.27	461.21
Stewart, Burkhardt and Voo	670.12	460.81
This Study:		
Method I	904.31	570.58
Method II	760.23	449.83
Method III	407.01	389.66
Method IV	604.17	456.47

TABLE H2 -- Continued

Mixture 20		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	664.09	364.65
Van der Waal-Berthelot (Intermediate Virial)	670.46	372.35
Berthelot (Virial)	690.33	379.54
Kay	669.54	368.35
Leland and Mueller	674.28	370.86
Joffe	675.45	371.55
Stewart, Burkhardt and Voo	676.21	371.76
This Study:		
Method I	804.42	412.99
Method II	717.47	368.35
Method III	495.94	336.94
Method IV	636.85	370.11

TABLE H2 -- Continued

Mixture 21		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	662.70	368.86
Van der Waal-Berthelot (Intermediate Virial)	669.35	377.91
Berthelot (Virial)	693.40	386.74
Kay	669.38	373.17
Leland and Mueller	682.68	381.56
Joffe	683.88	382.44
Stewart, Burkhardt and Voo	684.61	382.64
This Study:		
Method I	734.92	375.62
Method II	730.13	373.17
Method III	481.08	335.92
Method IV	634.79	375.41

TABLE H2 -- Continued

Mixture 22		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	670.77	374.30
Van der Waal-Berthelot (Intermediate Virial)	678.45	383.58
Berthelot (Virial)	701.63	392.17
Kay	677.59	379.23
Leland and Mueller	682.68	381.56
Joffe	683.88	382.44
Stewart, Burkhardt and Voo	684.61	382.64
This Study:		
Method I	846.75	438.19
Method II	732.81	379.23
Method III	529.10	355.19
Method IV	643.86	384.29

TABLE H2 -- Continued

Mixture 23		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	669.29	355.91
Van der Waal-Berthelot (Intermediate Virial)	673.31	360.47
Berthelot (Virial)	685.32	364.75
Kay	672.22	358.11
Leland and Mueller	674.32	359.19
Joffe	675.66	359.81
Stewart, Burkhardt and Voo	676.48	360.02
This Study:		
Method I	766.78	392.05
Method II	700.39	358.11
Method III	552.66	335.97
Method IV	653.26	359.31

TABLE H2 -- Continued

Mixture 24		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	658.74	381.53
Van der Waal-Berthelot (Intermediate Virial)	666.03	395.26
Berthelot (Virial)	705.26	410.08
Kay	670.74	388.18
Leland and Mueller	678.09	393.36
Joffe	678.16	394.50
Stewart, Burkhardt and Voo	678.75	394.67
This Study:		
Method I	912.51	478.52
Method II	740.24	388.18
Method III	379.04	325.59
Method IV	600.74	391.54

TABLE H2 -- Continued

Mixture 25		
Combination Rule	$P_{c_{mix}}$	$T_{c_{mix}}$
Empirical Statistical	673.77	355.08
Van der Waal-Berthelot (Intermediate Virial)	677.50	358.33
Berthelot (Virial)		360.89
Kay	675.14	356.80
Leland and Mueller	676.43	357.08
Joffe	677.99	357.63
Stewart, Burkhardt and Voo		357.85
This Study:		
Method I	743.88	380.20
Method II	698.10	356.80
Method III	648.44	352.25
Method IV	669.81	356.93

APPENDIX I

1. EXPERIMENTAL CRITICAL PROPERTIES FOR VOLATILE HYDROCARBON MIXTURES
2. COMPOSITION OF MIXTURES

TABLE I1

EXPERIMENTAL CRITICAL TEMPERATURES AND PRESSURES

FOR VOLATILE HYDROCARBON MIXTURES

BINARY MIXTURES

Ethane-η-Butane Mixtures[a]			
Eykman Molecular Refraction	Molecular Weight	Critical Temperature (°F)	Critical Pressure (Psia)
41.324	53.2	283.1	646.1
35.585	45.4	237.4	780.8
31.319	39.6	191.2	841.6
27.935	35.0	147.6	827.2
25.360	31.5	108.4	759.2

Ethane-η-Heptane Mixtures[b]			
62.071	81.4	468.2	682.0
45.518	58.9	373.9	1106.0
36.027	46.0	276.8	1263.0
30.068	37.9	189.8	1132.0
25.875	32.2	120.3	850.0

[a]Kay, Ind. Eng. Chem., 32, 353 (1940).

[b]Kay, Ibid, 30, 459 (1938).

TABLE I1 -- Continued

BINARY MIXTURES

Eykman Molecular Refraction	Molecular Weight	Critical Temperature (°F)	Critical Pressure (Psia)
Propane-η-Butane Mixtures[c]			
42.722	55.1	290.4	588.0
41.398	53.3	280.2	609.0
39.559	50.8	264.4	630.0
37.646	48.2	243.5	638.0
36.027	46.0	224.4	631.0
Propane-η-Pentane Mixtures[d]			
47.946	62.2	339.0	608.0
43.678	56.4	300.9	648.0
38.823	49.8	255.8	671.0
38.234	49.0	250.4	664.0

[c]Nysewander, Sage and Lacey, Ind. Eng. Chem., 32, 118 (1940).

[d]Sage and Lacey, Ibid., 32, 992 (1940).

TABLE I1 -- Continued

BINARY MIXTURES

Eykman Molecular Refraction	Molecular Weight	Critical Temperature (°F)	Critical Pressure (Psia)
η-Pentane-η-Heptane Mixtures[e]			
64.278	84.4	450.0	422.5
60.379	79.1	427.0	477.5
70.531	92.9	488.0	475.0
Methane-Propane Mixtures[f]			
32.496	41.2	196.0	765.0
30.436	38.4	178.3	890.0
28.376	35.6	159.7	1020.0
26.316	32.8	138.8	1160.0
24.256	30.0	115.4	1293.0
22.196	27.2	88.0	1408.0
20.136	24.4	50.7	1469.0

[e]Cummings, Stone and Volante, Ind. Eng. Chem., 25, 728 (1933).

[f]Sage, Schaafsma and Lacey, Ibid., 26, 214 (1934).

TABLE I1 -- Continued

BINARY MIXTURES

Methane-η-Butane Mixtures[g]			
Eykman Molecular Refraction	Molecular Weight	Critical Temperature (°F)	Critical Pressure (Psia)
35.954	45.9	266.0	1093.0
30.142	38.0	217.7	1537.0
26.022	32.4	163.9	1799.0
23.005	28.3	110.1	1901.0
20.651	25.1	59.2	1924.0

[g]Sage, Hicks and Lacey, Ind. Eng. Chem., 32, 1085 (1940).

TABLE I1 -- Continued

COMPLEX MIXTURES*

Eykman Molecular Refraction	Mixture	Molecular Weight	Critical Temperature (°F)	Critical Pressure (Psia)
20.578	S-2	25.0	55.0	2387.0
23.888	S-3	29.5	109.0	2574.0
23.594	S-4	29.1	109.0	2537.0
28.744	S-5	36.1	169.5	2615.0
20.210	T-1	24.5	54.0	2605.0
20.945	T-3	25.5	65.0	2675.0
22.490	T-4	27.6	90.0	2730.0
29.921	T-5	37.7	189.0	2900.0
22.343	B-1	27.4	78.0	1826.0
23.962	B-2	29.6	116.0	1797.0
25.139	B-3	31.2	142.0	1796.0
26.169	B-4	32.6	149.5	1706.0

*See Compositions and Properties on Page .

TABLE I1 -- Continued

COMPOSITIONS AND PROPERTIES OF MIXTURES INVESTIGATED

Compound	Mixture S-2 mol.%	Mixture S-3 mol.%	Mixture S-4 mol.%	Mixture S-5 mol.%
Nitrogen	0.58	0.53	0.54	59.70
Methane	78.80	62.40	72.80	8.90
Ethane	5.90	5.42	5.46	8.90
Propane	3.15	3.00	3.02	5.00
Butanes	2.66	3.10	2.07	4.90
Pentanes	4.25	7.10	6.88	9.30
Hexanes	2.52	4.56	4.38	12.20
Heptanes +	2.14	3.88	3.75	

	Mixture T-1 mol.%	Mixture T-3 mol.%	Mixture T-4 mol.%	Mixture T-5 mol.%
Nitrogen	0.38	0.38	0.36	0.30
Carbon Dioxide	0.45	0.44	0.43	0.35
Methane	83.00	81.5	78.40	64.30
Ethane	3.76	3.72	3.55	2.94
Propane	1.44	1.41	1.36	1.11
Butanes	0.89	1.02	1.30	2.52
Pentanes	4.36	5.01	6.31	12.30
Hexanes	3.08	3.54	4.47	8.71
Heptanes +	2.63	3.03	3.82	7.47

TABLE I1 -- Continued

COMPOSITIONS AND PROPERTIES OF MIXTURES INVESTIGATED

Compound	Mixture B-1 mol.%	Mixture B-2 mol.%	Mixture B-3 mol.%	Mixture B-4 mol.%
Nitrogen	0.33	0.30	0.28	0.27
Carbon Dioxide	0.38	0.35	0.34	0.32
Methane	70.65	65.24	61.30	58.25
Ethane	3.23	2.98	2.80	2.66
Propane	1.22	1.13	1.06	1.01
Butanes	24.20	30.00	34.22	37.50

APPENDIX J

SAMPLE COMPRESSIBILITY CHART

ERROR ANALYSIS

TABLE J

COMPRESSIBILITY CHART NO. 1

SAMPLE CURVE FIT AND ERROR ANALYSIS

Reduced Pressure, $P_R = 2.0$

T_R	Z (Exp.)	Z (Calc.)	Per Cent Deviation
0.8590	0.4632	0.4743	2.391
0.8800	0.4941	0.4935	-0.114
0.9460	0.5372	0.5510	2.578
0.9900	0.5869	0.5868	-0.003
1.0460	0.5762	0.6295	9.260
1.0520	0.6606	0.6339	-4.036
1.1000	0.7064	0.6676	-5.490
1.1240	0.6297	0.5835	8.553
1.1310	0.7506	0.6880	-8.327
1.1470	0.7154	0.6982	-2.394
1.1630	0.7130	0.7081	-0.675
1.2080	0.7714	0.7346	-4.767
1.2150	0.7286	0.7385	1.365
1.2510	0.7393	0.7579	2.518
1.2590	0.7386	0.7620	3.173
1.2700	0.8111	0.7675	-5.363
1.2800	0.7819	0.7725	-1.196
1.2800	0.8533	0.7725	-9.464
1.3070	0.7420	0.7853	5.845
1.3090	0.7944	0.7862	-1.020
1.3450	0.8207	0.8021	-2.261
1.3560	0.8008	0.8067	0.737
1.3640	0.7861	0.8099	3.034
1.3730	0.7848	0.8135	3.660
1.3790	0.8957	0.8158	-8.913
1.3840	0.7373	0.8177	10.915
1.3860	0.8090	0.8185	1.179
1.3900	0.8162	0.8200	0.471
1.4030	0.7755	0.8248	6.360
1.4050	0.8172	0.8255	1.021
1.4340	0.8225	0.8355	1.582
1.4400	0.8391	0.8374	-0.194
1.4440	0.8243	0.8387	1.753
1.4540	0.8427	0.8418	-0.097
1.4560	0.8431	0.8424	-0.071
1.4680	0.8168	0.8460	3.585
1.4790	0.8543	0.8492	-0.590

TABLE J1 -- Continued

T_R	Z (Exp.)	Z (Calc.)	Per Cent Deviation
1.4910	0.7996	0.8525	6.623
1.5050	0.8424	0.8562	1.641
1.5070	0.8546	0.8567	0.249
1.5080	0.8923	0.8569	-3.957
1.5160	0.8714	0.8589	-1.426
1.5190	0.8936	0.8596	-3.794
1.5320	0.8762	0.8627	-1.538
1.5460	0.8537	0.8657	1.416
1.5530	0.8799	0.8672	-1.437
1.5560	0.8774	0.8678	-1.087
1.5850	0.8749	0.8732	-0.186
1.6250	0.8831	0.8792	-0.431
1.6660	0.9011	0.8837	-1.927

Average error = 0.1829 per cent

Average absolute error = 3.0138 per cent

$Z = 0.7071 + 0.18228\ T_R - 0.52096\ T_R^2$

TABLE J2

COMPRESSIBILITY CHART NO. 2

SAMPLE CURVE FIT AND ERROR ANALYSIS

Reduced Pressure, $P_R = 2.0$

T_R	Z (Exp.)	Z (Calc.)	Per Cent Deviation
1.190	0.6179	0.6285	1.722
1.266	0.7809	0.6801	-12.909
1.274	0.7043	0.6852	- 2.710
1.306	0.7331	0.7051	- 3.819
1.316	0.7432	0.7111	- 4.315
1.333	0.7631	0.7212	- 5.496
1.334	0.6856	0.7217	5.271
1.338	0.7618	0.7241	- 4.954
1.365	0.7591	0.7393	- 2.605
1.372	0.7457	0.7432	- 0.339
1.375	0.7853	0.7448	- 5.156
1.384	0.7858	0.7497	- 4.598
1.393	0.7384	0.7545	2.174
1.394	0.7790	0.7550	- 3.083
1.399	0.7375	0.7576	2.726
1.408	0.7320	0.7623	4.134
1.412	0.7574	0.7643	0.913
1.418	0.7913	0.7674	- 3.026
1.422	0.8127	0.7694	- 5.332
1.427	0.8142	0.7719	- 5.200
1.445	0.8237	0.7806	- 5.227
1.446	0.7596	0.7811	2.834
1.446	0.7950	0.7811	- 1.745
1.455	0.8250	0.7854	- 4.800
1.465	0.8156	0.7901	- 3.131
1.486	0.8427	0.7996	- 5.119
1.491	0.8263	0.8018	- 2.970
1.491	0.8333	0.8018	- 3.785
1.498	0.8510	0.8048	- 5.429
1.501	0.8005	0.8061	0.699
1.506	0.8424	0.8082	- 4.057
1.511	0.8569	0.8103	- 5.434
1.512	0.8141	0.8108	- 0.411
1.516	0.8566	0.8124	- 5.157
1.516	0.8575	0.8124	- 5.257

TABLE J2 -- Continued

T_R	Z (Exp.)	Z (Calc.)	Per Cent Deviation
1.519	0.8317	0.8137	- 2.169
1.520	0.8146	0.8141	- 0.064
1.522	0.8278	0.8149	- 1.559
1.529	0.8478	0.8177	- 3.545
1.540	0.8482	0.8221	- 3.075
1.544	0.8494	0.8237	- 3.027
1.564	0.8740	0.8313	- 4.886
1.566	0.8576	0.8320	- 2.981
1.575	0.8811	0.8353	- 5.196
1.578	0.8691	0.8364	- 3.763
1.587	0.8749	0.8396	- 4.036
1.592	0.8818	0.8413	- 4.590
1.618	0.8906	0.8500	- 4.558
1.620	0.8802	0.8506	- 3.358
1.627	0.8798	0.8529	- 3.062
1.641	0.8952	0.8572	- 4.249
1.667	0.9012	0.8647	- 4.053
1.699	0.9067	0.8731	- 3.709
1.703	0.8843	0.8741	- 1.158
1.710	0.9032	0.8757	- 3.040
1.734	0.9040	0.8812	- 2.524
1.742	0.9015	0.8829	- 2.065

Average error = 2.92 per cent

Average absolute error = 3.64 per cent

$Z = 0.8672 + 1.8008\ T_R - 0.4570\ T_R^2$

TABLE J3

COMPRESSIBILITY CHART NO. 3

SAMPLE CURVE FIT AND ERROR ANALYSIS

Reduced Pressure, $P_R = 2.0$

T_R	Z (Exp.)	Z (Calc.)	Per Cent Deviation
1.125	0.5148	0.5453	5.930
1.258	0.5822	0.6626	13.813
1.266	0.6649	0.6690	0.616
1.339	0.7656	0.7235	- 5.494
1.347	0.7918	0.7291	- 7.916
1.362	0.7746	0.7394	- 4.546
1.364	0.6941	0.7407	6.719
1.371	0.7562	0.7454	- 1.427
1.386	0.7118	0.7552	6.102
1.391	0.8045	0.7585	- 5.724
1.406	0.7894	0.7679	- 2.722
1.411	0.8116	0.7710	- 5.002
1.419	0.8359	0.7759	- 7.179
1.432	0.8141	0.7837	- 3.739
1.445	0.8319	0.7912	- 4.888
1.450	0.8323	0.7941	- 4.591
1.454	0.8163	0.7964	- 2.444
1.465	0.8446	0.8025	- 4.987
1.467	0.7927	0.8036	1.372
1.483	0.8438	0.8122	- 3.747
1.491	0.8691	0.8164	- 6.068
1.493	0.8426	0.8174	- 2.991
1.504	0.8480	0.8230	- 2.948
1.516	0.8117	0.8289	2.125
1.521	0.8664	0.8314	- 4.043
1.527	0.8673	0.8342	- 3.811
1.529	0.8488	0.8352	- 1.603
1.536	0.8459	0.8385	- 0.878
1.538	0.8721	0.8394	- 3.750
1.540	0.8161	0.8403	2.967
1.543	0.8213	0.8417	2.482
1.544	0.8346	0.8435	1.066
1.547	0.8346	0.8435	1.066
1.548	0.8117	0.8439	3.973
1.573	0.8743	0.8548	- 2.230
1.596	0.8907	0.8641	- 2.984

TABLE J3 -- Continued

T_R	Z (Exp.)	Z (Calc.)	Per Cent Deviation
1.604	0.8274	0.8672	4.811
1.605	0.8956	0.8676	- 3.128
1.608	0.8807	0.8687	- 1.360
1.614	0.8556	0.8710	1.795
1.621	0.8545	0.8735	2.226
1.622	0.8576	0.8739	1.898
1.626	0.8607	0.8753	1.697
1.653	0.8986	0.8844	- 1.576
1.662	0.8776	0.8873	1.104
1.667	0.8569	0.8888	3.726
1.683	0.8305	0.8936	7.592
1.684	0.8604	0.8938	3.886
1.697	0.8789	0.8974	2.108
1.742	0.9032	0.9083	0.563
1.796	0.8880	0.9181	3.386
1.808	0.8991	0.9198	2.298
1.816	0.9048	0.9208	1.768
1.860	0.9236	0.9251	0.160
1.881	0.9226	0.9263	0.401
1.886	0.8932	0.9265	3.729
1.908	0.9117	0.9271	1.687
2.026	0.9423	0.9201	- 2.355
2.037	0.9302	0.9186	- 1.247
2.139	0.9316	0.8976	- 3.650

Average error = 0.80 per cent

Average absolute error = 4.26 per cent

$$Z = -1.3054 + 2.3277\ T_R - 0.6067\ T_R^2$$

TABLE J4

COMPRESSIBILITY CHART NO. 4

SAMPLE CURVE FIT AND ERROR ANALYSIS

Reduced Pressure, $P_R = 2.0$

T_R	Z (Exp.)	Z (Calc.)	Per Cent Deviation
1.058	0.4637	0.4882	5.281
1.073	0.4749	0.5068	6.713
1.161	0.6322	0.6073	- 3.933
1.183	0.5913	0.6302	6.581
1.191	0.6271	0.6383	1.787
1.232	0.6995	0.6779	- 3.088
1.255	0.6379	0.6987	9.537
1.274	0.7461	0.7152	- 4.142
1.293	0.7582	0.7310	- 3.589
1.299	0.7738	0.7358	- 4.907
1.305	0.7567	0.7406	- 2.126
1.312	0.7381	0.7461	1.084
1.314	0.7321	0.7477	2.124
1.323	0.7617	0.7545	- 0.940
1.339	0.7881	0.7664	- 2.752
1.362	0.7082	0.7826	10.511
1.372	0.7663	0.7894	3.012
1.375	0.8040	0.7914	- 1.571
1.379	0.8116	0.7940	- 2.169
1.380	0.7785	0.7946	2.074
1.382	0.8135	0.7959	- 2.158
1.385	0.7628	0.7979	4.598
1.395	0.7733	0.8042	3.994
1.399	0.8063	0.8067	0.045
1.405	0.7783	0.8103	4.114
1.409	0.8267	0.8127	- 1.692
1.411	0.8074	0.8139	0.806
1.427	0.7818	0.8231	5.288
1.438	0.8078	0.8292	2.650
1.439	0.8140	0.8298	1.935
1.444	0.8315	0.8324	0.111
1.445	0.8122	0.8330	2.556
1.445	0.8384	0.8330	- 0.649
1.451	0.8169	0.8361	2.349
1.466	0.8556	0.8436	- 1.398

TABLE J4 -- Continued

T_R	Z (Exp.)	Z (Calc.)	Per Cent Deviation
1.469	0.8344	0.8451	1.283
1.474	0.8628	0.8475	- 1.774
1.474	0.8460	0.8475	0.177
1.483	0.8419	0.8517	1.163
1.492	0.8197	0.8557	4.395
1.492	0.8314	0.8557	2.926
1.513	0.8310	0.8646	4.039
1.517	0.8440	0.8662	2.625
1.517	0.8518	0.8662	1.685
1.517	0.8368	0.8662	3.508
1.519	0.8442	0.8669	2.694
1.519	0.8661	0.8669	0.097
1.524	0.8502	0.8689	2.196
1.546	0.8498	0.8768	3.175
1.547	0.8732	0.8771	0.449
1.559	0.8752	0.8810	0.667
1.564	0.8877	0.8826	- 0.575
1.565	0.8891	0.8829	- 0.698
1.586	0.8603	0.8889	3.320
1.594	0.8817	0.8909	1.046
1.594	0.8905	0.8909	0.047
1.599	0.8761	0.8921	1.831
1.629	0.8801	0.8985	2.091
1.666	0.8930	0.9040	1.235
1.679	0.9020	0.9054	0.373
1.685	0.9189	0.9059	- 1.418
1.698	0.8902	0.9067	1.858
1.712	0.9035	0.9073	0.423
1.719	0.9105	0.9075	- 0.332

Average error = 1.26 per cent

Average absolute error = 2.51 per cent

$$Z = - 1.8857 + 3.2344\ T_R - 0.9363\ T_R^2$$

APPENDIX K

DENSITY CORRELATION

(a) DATA

(b) SAMPLE CALCULATION

TABLE K1

CALCULATED REFRACTIVE INDICES AND DIMENSIONLESS

REFRACTIVE INDEX FUNCTIONS UP TO THE CRITICAL POINT

Temperature °F	n-Heptane		n-Octane	
	Refractive Index n	Dimensionless Function $(n^2-1)/(n+0.4)$	Refractive Index n	Dimensionless Function $(n^2-1)/(n+0.4)$
32.00	1.397803	0.53056	1.407186	0.54237
50.00	1.392636	0.52405	1.402327	0.53626
68.00	1.387716	0.51784	1.397473	0.53015
77.00	1.385138	0.51458	1.395078	0.52713
86.00	1.382622	0.51140	1.392684	0.52411
104.00	1.377594	0.50504	1.387960	0.51815
122.00	1.372452	0.49853	1.383062	0.51196
140.00	1.367077	0.49171	1.378110	0.50569
158.00	1.361412	0.48452	1.372926	0.49913
176.00	1.355754	0.47732	1.367808	0.49264
194.00	1.350045	0.47005	1.362696	0.48615
212.00	1.344284	0.46271	1.357353	0.47936
230.00	-	-	1.351957	0.47249
248.00	-	-	1.346332	0.46532
512.60*	1.127782	0.17796	-	-
565.16*	-	-	1.127326	0.17734

*Refers to values at the critical point.

TABLE K1 -- Continued

Temperature °F	n-Nonane		n-Decane	
	Refractive Index n	Dimensionless Function $(n^2-1)/(n+0.4)$	Refractive Index n	Dimensionless Function $(n^2-1)/(n+0.4)$
32.00	1.414895	0.55205	1.421077	0.55981
50.00	1.410040	0.54596	1.416405	0.55395
68.00	1.405370	0.54009	1.416405	0.55395
77.00	1.403097	0.53723	1.409646	0.72630
86.00	1.400765	0.53429	1.407315	0.54253
104.00	1.396164	0.52850	1.402837	0.53690
122.00	1.391509	0.52263	1.398304	0.53119
140.00	1.386739	0.51661	1.393716	0.52541
158.00	1.381797	0.51036	1.389014	0.51948
176.00	1.377038	0.50434	1.384436	0.51369
194.00	1.372225	0.49824	1.379743	0.50776
212.00	1.367240	0.49192	1.374997	0.50175
230.00	1.362202	0.48552	1.370197	0.49567
248.00	1.356992	0.47890	1.365284	0.48944
266.00	1.351493	0.47190	1.360259	0.48305
284.00	1.346179	0.46512	1.355299	0.47674
302.00	1.340872	0.45835	1.350109	0.47013
320.00	-	-	1.344749	0.46330
338.00	-	-	1.339162	0.45617
611.60*	1.127529	0.17762	-	-
654.80*	-	-	1.127249	0.17724

*Refers to values at the critical point.

TABLE K1 -- Continued

Temperature °F	n-Undecane		n-Dodecane	
	Refractive Index n	Dimensionless Function $(n^2-1)/(n+0.4)$	Refractive Index n	Dimensionless Function $(n^2-1)/(n+0.4)$
32.00	1.426208	0.56623	1.430542	0.57166
50.00	1.421659	0.56054	1.426055	0.56604
68.00	1.417174	0.55491	1.421573	0.56043
77.00	1.415023	0.55222	1.419483	0.55781
86.00	1.412754	0.54937	1.417334	0.55511
104.00	1.408338	0.54382	1.413040	0.54972
122.00	1.403926	0.53827	1.408690	0.54426
140.00	1.399519	0.53272	1.404344	0.53880
158.00	1.394938	0.52695	1.399883	0.53318
176.00	1.390480	0.52133	1.395428	0.52757
194.00	1.385968	0.51563	1.391154	0.52218
212.00	1.381342	0.50978	1.386648	0.51649
230.00	1.376721	0.50394	1.382147	0.51080
248.00	1.371927	0.49786	1.377473	0.50489
266.00	1.367139	0.49179	1.372863	0.49905
284.00	1.362357	0.48572	1.368258	0.49321
302.00	1.357462	0.47950	1.363540	0.48722
320.00	1.352455	0.47312	1.358711	0.48108
338.00	1.347278	0.46653	1.353827	0.47487
356.00	1.341990	0.45978	1.348891	0.46858
374.00	1.336533	0.45281	1.343785	0.46207
392.00	-	-	1.338452	0.45526
410.00	-	-	1.332774	0.44800

TABLE K1 -- Continued

Temperature °F	n-Undecane		n-Dodecane	
	Refractive Index n	Dimensionless Function $(n^2-1)/(n+0.4)$	Refractive Index n	Dimensionless Function $(n^2-1)/(n+0.4)$
692.60*	1.127569	0.17767	-	-
726.80*	-	-	1.127369	0.17740

*Refers to values at the critical point.

TABLE K2

DENSITY CORRELATION DATA

SAMPLE CALCULATION

Find the density of nonane at 122°F (50°C) and 5000 psia.

$T_R = 0.542$

$P_R = 15.11$

EMR = 96.5376

MW = 128.25

From Figure 8-2,

$(n^2-1)/(n+0.4) \cong 0.498$

From Figure 8-3,

$\rho/((n^2-1)/(n+0.4)) = 1.385$

$\rho = 0.6897$ g/ml

Find the density of an unknown normal hydrocarbon liquid mixture at 122°F (50°C) and 5000 psia.

(a) Measure the density at atmospheric conditions.

(b) Obtain EMR from Figure 6-4.

(c) Get reduced temperature and pressure from either Figures 7-1 and 7-2, or Figures 7-7 or 7-8.

(d) From Figure 8-2 obtain $(n^2-1)/(n^2+0.4)$ by interpolating between the EMR or MW values of the pertinent pure compounds.

(e) Enter Figure 8-3 and compute the value of ρ at the required conditions.

APPENDIX L

COMPRESSIBILITY CHART

CORRELATION SAMPLE CALCULATIONS

TABLE L1

CORRELATION SAMPLE CALCULATIONS

Method 1

Component	X_i	X_i^*	EMR	$(X_i^*)(EMR)$
N_2	0.0046	0.0047	9.407	0.0433
CO_2	0.0030	0.0031	15.750	0.0488
H_2S	0.1438	0.1448	19.828	2.8704
nC_1	0.8414	0.8475	13.984	11.8514
	0.9928	1.0000		14.8139
nC_2	0.0059	0.8194	23.913	19.5943
nC_3	0.0008	0.1111	34.316	3.8125
iC_4	0.0003	0.0417	44.741	1.8657
nC_5	0.0002	0.0278	44.243	1.2300
	0.0072	1.0000		26.5025

$EMR_1 = 14.8139$

$EMR_2 = 26.5025$

$(T_c/P_c)_1$ 0.506 (Figure 7-1)

$(T_c/P_c)_2$ 0.845 (Figure 7-1)

$T_c/P_c = (0.9928)(0.506) + (0.0072)(0.845)$

$T_c/P_c = 0.5124$

TABLE L1 -- Continued

$T_c/P_c = 0.5124$

$T_c/\sqrt{P_c} = 14.044$ (Figure 7-2)

$T_c = 384.9$ °R

$P_c = 751.2$ PSIA

$P_{exp} = 2021.3$ PSIA $P_R = 2.690$

$T_{exp} = 595.0$ °R $T_R = 1.546$

$Z_{exp} = 0.8338$

Z (Figure 7-3) = 0.840

Method 2

$T_c = 392.42$ °R (By Kay's Combination Rule)

$T_c/P_c = 0.5124$ (As in Method 1)

$P_c = 765.85$ PSIA

$P_{exp} = 2021.3$ $P_R = 2.639$

$T_{exp} = 595$ °R $T_R = 1.516$

$Z_{exp} = 0.8338$

Z (Figure 7-3) = 0.830

TABLE L1 -- Continued

Method 3

Component	X_i	X_i^*	EMR	$(X_i^*)(EMR)$
N_2	0.0046	0.6053	9.407	5.694
CO_2	0.0030	0.3947	15.750	6.217
	0.0076	1.0000		11.911
H_2S	0.1438	0.1460	19.828	2.895
nC_1	0.8414	0.8540	13.984	11.942
	0.9852	1.0000		14.837
nC_2	0.0059	0.8194	23.913	19.594
nC_3	0.0008	0.1111	34.316	3.813
nC_4	0.0002	0.0278	44.243	1.230
iC_4	0.0003	0.0417	44.741	1.866
	0.0072	1.0000		26.503

$EMR_1 = 11.911$

$EMR_2 = 14.837$

$EMR_3 = 26.503$

Molecular Weight	(Figure 6-2)
$MW_1 = 33.4$	Curve 1
$MW_2 = 18.7$	Curve 2

TABLE L1 -- Continued

$MW_3 = 33.0$ Curve 3

$MW_{mix} = (33.4)(0.0076) + (18.7)(0.9852)$
$+ (33.0)(0.0072) = 19.3899$

$\sqrt{MW}_{mix} = 4.4034$

$T_c/P_c^{1/3}$ (Figure 7-8)

$(T_c/P_c^{1/3})_1 = 38.2$ Curve 1

$(T_c/P_c^{1/3})_2 = 42.0$ Curve 2

$(T_c/P_c^{1/3})_3 = 66.0$ Curve 3

$(T_c/P_c^{1/3})_{mix} = (38.2)(0.0076) + (42.0)(0.9852) +$
$+ (66.0)(0.0072) = 42.1439$

$X_i = T_c^{5/6} \sqrt{MW}/5.665\ P_c^{1/3}$ (Figure 7-7)

$X_i = 13.9$ Curve 1

$X_2 = 12.5$ Curve 2

$X_3 = 22.5$ Curve 3

$X_{mix} = (13.9)(0.0076) + (12.5)(0.9852) + (22.5)(0.0072)$

$X_{mix} = 12.583$

$P_c^{1/3} = T_c^{5/6} \sqrt{MW}/(5.665)(X)$

$P_c^{1/3} = T_c^{5/6}\ (0.0585)$

TABLE L1 -- Continued

$P_c^{1/3} = T_c/42.1439$

$T_c^{1/6} = 2.604$

$T_c = 311.78\ °R$

$P_c^{1/3} = 7.398$

$P_c = 404.9$ PSIA

$P_{exp} = 2021.3$ $\qquad$ $P_R = 4.992$

$T_{exp} = 595°R$ $\qquad$ $T_R = 1.908$

$Z_{exp} = 0.8338$

Z (Figure 7-5) = 0.8451

Method 4

Using the same grouping as in Method 3 we obtain:

$EMR_1 = 11.911$

$EMR_2 = 14.837$

$EMR_3 = 26.503$

Molecular Weight	(Figure 6-2)
$MW_1 = 33.8$	Curve 1
$MW_2 = 18.7$	Curve 2
$MW_3 = 33.0$	Curve 3

$MW_{mix} = 19.3899$

$\sqrt{MW}_{mix} = 4.4034$

TABLE L1 -- Continued

T_{c_1} = 355°R Curve 1
T_{c_2} = 405°R Curve 2 (Figure 7-9)
T_{c_3} = 580°R Curve 3

$T_{c_{mix}}$ = (0.0076)(355) + (0.9852)(405)
+ (0.0072)(580) = 405.88°R

$X = (T_{c_{mix}})^{5/6} \sqrt{MW}/(P_c^{1/3})$ (5.665)

X = 12.583

$(P_c)^{1/3}_{mix} = (0.0618\ T_c^{5/6})$

P_c = 782.88 PSIA

P_{exp} = 2021.3 PSIA P_R = 2.582

T_{exp} = 595°R T_R = 1.466

Z_{exp} = 0.8338

Z (Figure 7-6) = 0.8200

APPENDIX M

COMPUTER PROGRAMS

COMPUTER PROGRAM NO. 1

```
*C      MOLECULAR WEIGHT-EMR CORRELATION
*C      LEAST SQUARES FOR LINEAR EQUATIONS
*C      X REPRESENTS EYKMAN MOLECULAR REFRACTION
*C      Y REPRESENTS MOLECULAR WEIGHT
*       DIMENSIONC(2,3)
*1      READ10,N
*       DO2I=1,2
*       DO2J=1,3
*2      C(I,J)=0.
*       DO3K=1,N
*       READ20,X,Y
*       DO3I=1,2
*       C(I,3)=C(I,3)+Y*X**(I-1)
*       DO3J=1,2
*3      C(I,J)=C(I,J)+X**(I+J-2)
*       D=C(1,1)*C(2,2)-C(1,2)*C(2,1)
*       A=(C(1,3)*C(2,2)-C(1,2)*C(2,3))/D
*       B=(C(1,1)*C(2,3)-C(1,3)*C(2,1))/D
*       PRINT20,A,B
*       SUM=0.
*       SABS=0.
*C      READ IN THE SAME SET OF DATA FOR AN ERROR ANALYSIS
*       READ10,N
*       DO41=1,N
*       READ20,X,Y
*       YCALC=A+B*X
*       ERR=(Y-YCALC)/Y*100.
*       SUM=SUM+ERR
*       SABS=SABS+ABS(ERR)
*4      PRINT30,I,X,Y,YCALC,ERR
*       AN=N
*       SUM=SUM/AN
*       SABS=SABS/AN
```

COMPUTER PROGRAM NO. 1 -- Continued

```
*          PRINT20,SUM,SABS
*          GOTO1
*10        FORMAT(15)
*20        FORMAT(F9.3,F12.4)
*30        FORMAT(15,F16.5,F16.5,F16.5,F16.5)
*          STOP
*          END
```

COMPUTER PROGRAM NO. 2

```
C       COMBINATION RULES - THEOREM OF CORRESPONDING STATES
C       PROGRAM *****BY WILFRED R MC LEOD
C       C ***********COMPONENT IDENTIFICATION
C       X ***********MOL FRACTION OF COMPONENT
C       PC **********CRITICAL PRESSURE OF COMPONENT
C       TC **********CRITICAL TEMPERATURE OF COMPONENT
C       ZC **********CRITICAL COMPRESSIBILITY FACTOR OF COMPONENT
C       N  **********NUMBER OF COMPONENTS
C       SPK *********NUMBER OF THE MIXTURE_
C       ALL OTHER TERMS ARE SELF-EXPLANATORY
        READ 26,P.T
        DEVS=0.
        PUNCH 30
      2 READ 27,SPK
        READ 29,N
        DIMENSION C(12),X(12),PC(12),TC(12),ZC(12)
        PUNCH 32,SPK
        PUNCH 35
        PUNCH 36
        T=T+459.7
        DO 1 I=1,N
        READ 25,C(I),X(I),PC(I),TC(I),ZC(I)
      1 PUNCH 37,C(I),X(I),PC(I),TC(I),ZC(I)
        TCK=0.
        PCK=0.
        DO 6 I=1,N
        TCK=TCK+X(I)*TC(I)
      6 PCK=PCK+X(I)*PC(I)
        S=(T*PCK)/(P*TCK)
        IF(S-1.90)3,3,5
      3 IF(S-.5)7,7,8
      5 ALPH=(7.-S)/5.
        GO TO 9
```

COMPUTER PROGRAM NO. 2 -- Continued

```
 7 ALPH=(2.07-S)/.714
   GO TO 9
 8 ALPH=(3.28-S)/(1.35)
 9 IF(ALPH-1.)11,11,13
11 ALPH=1.0
13 SUMJA=0.
   SUMJB=0.
   SUMSB=0.
   SUMSC=0.
   SUMK=0.
   SUMZ=0.
   SUML=0.
   DO 12  I=1,N
   SUMJA=SUMJA+X(I)*TC(I)/PC(I)**.5
   SUMSB=SUMSB+X(I)*TC(I)/PC(I)
   SUMSC=SUMSC+X(I)*(TC(I)/PC(I))**.5
   A=X(I)*(ZC(I)*TC(I)**(ALPH+1.)/PC(I))**.5
   D=.5*(ZC(I)*TC(I)/PC(I))**.333
   DJ=(TC(I)/PC(I))**.333
   DO 10  J=1,N
   B=X(J)*(ZC(J)*TC(J)**(ALPH+1.)/PC(J))**.5
   F=.5*(ZC(J)*TC(J)/PC(J))**.333
   FJ=(TC(J)/PC(J))**.333
   SUMK=SUMK+A*B
   SUMJB=SUMJB+X(I)*X(J)*(DJ+FJ)**3./8.
10 SUML=SUML+X(I)*X(J)*(D+F)++3.
12 SUMZ=SUMZ+ZC(I)*X(I)
   B=(SUMSB+2.*SUMSC**2.)/3.
   TCM=(SUMK/SUML)**(1./ALPH)
   PCM=TCM*(SUMZ/SUML)
   TCJ=(SUMJA)**2./SUMJB
   PCJ=TCJ/SUMJB
   TCS=SUMJA**2./B
```

COMPUTER PROGRAM NO. 2 -- Continued

```
      PCS=TCS/B
      PUNCH 42
      PUNCH 53,TCK
      PUNCH 54,TCM
      PUNCH 55,TCJ
      PUNCH 56,TCS
      PUNCH 52
      PUNCH 43,PCK
      PUNCH 44,PCM
      PUNCH 45,PCJ
      PUNCH 46,PCS
   25 FORMAT(A3,F6.4,F8.2,F8.2,F6.4)
   26 FORMAT(F8.2,F8.2)
   27 FORMAT(A3)
   29 FORMAT(I3)
   30 FORMAT(9X,52HCOMBINATION RULES FOR PSEUDO-CRITICAL
      TEMPERATURE AN, 110HD PRESSURE)
   32 FORMAT(9X,30HGAS IDENTIFICATION MIXTURE NO-,A3/)
   35 FORMAT(10X,4HCOMP,5X,3HMOL,4X,8HCRITICAL,5X,8HCRITICAL,
      4X,5HCRITI,13HCAL)
   36 FORMAT(11X,2HNO,5X,4HFRAC,3X,10HPRESS PSIA,3X,10HTEMP
      DEG R,13X,11HCOMP FACTOR/)
   37 FORMAT(10X,A3,F10.4,F10.2,F13.2,F13.4)
   42 FORMAT(9X,36HPSEUDO-CRITICAL TEMPERATURES - DEG R/)
   43 FORMAT(9X,43HKAY **********************************,F8.2)
   44 FORMAT(9X,43HLELAND AND MEULLER ********************,F8.2)
   45 FORMAT(9X,43HJOFFE *********************************,F8.2)
   46 FORMAT(9X,43HSTEWART,BURKHARDT AND VOO **************,F8.2)
   52 FORMAT(9X,32HPSEUDO-CRITICAL PRESSURES - PSIA/)
   53 FORMAT(9X,43HKAY **********************************,F8.2)
   54 FORMAT(9X,43HLELAND AND MEULLER ********************,F8.2)
   55 FORMAT(9X,43HJOFFE *********************************,F8.2)
   56 FORMAT(9X,43HSTEWART,BURKHARDT AND VOO **************,F8.2)
```

COMPUTER PROGRAM NO. 2 -- Continued

```
GO TO 2
STOP
END
```

COMPUTER PROGRAM NO. 3

```
      DIMENSION C(12),X(12),PC(12),TC(12),ZC(12),W(12)
      DEVS=0.
      PUNCH 30
2     READ 27,SPK
      READ 26,N
      PUNCH 32,SPK
      PUNCH 35
      PUNCH 36
      T=T+459.7
      DO 1 I=1,N
      READ 25,C(I),X(I),PC(I),TC(I),ZC(I)
1     PUNCH 37,C(I),X(I),PC(I),TC(I),ZC(I)
      SUMJA=0.
      SUMSC=0.
      SUMV1=0.
      SUMV2=0.
      SUMB1=0.
      SUMB2=0.
      SUMSO=0.
      SUMSN=0.
      SUMSM=0.
      DO 10 I=1,N
      SUMJA=SUMJA+X(I)*TC(I)/PC(I)**.5
      SUMSC=SUMSC+X(I)*(TC(I)/PC(I))**.5
      DJ=(TC(I)/PC(I))**.333
      W(I)=ZC(I)*TC(I)/PC(I)
      SUMSO=SUMSO+X(I)*ZC(I)
      SUMV1=SUMV1+X(I)*TC(I)/PC(I)
10    SUMV2=SUMV2+X(I)*TC(I)**1.25/PC(I)**.5
      DO 12 I=1,N
      DO 12 J=1,N
      FJ=(TC(J)/PC(J))**.333
      SUMSM=SUMSM+X(I)*X(J)*(TC(I)*TC(J))**.5
      Q=X(I)*X(J)*((TC(I)/PC(I))**.3333+(TC(J)/PC(J))**.3333)**3./8.
```

COMPUTER PROGRAM NO. 3 -- Continued

```
      SUMB1=SUMB1+Q
      SUMB2=SUMB2+Q*TC(I)*TC(J)
12    SUMSN=SUMSN+X(I)*X(J)*(W(I)**.3333+W(J)**.3333)**3./8.
      B=(SUMV1+2.*SUMSC**2.)/3.
      TCSM=SUMSM
      PCSM=TCSM*SUMSO/SUMSN
      TCVD=(SUMV2**2/SUMV1)**.66667
      PCVD=TCVD/SUMV1
      TCB=(SUMB2/SUMB1)**.5
      PCB=TCB/SUMB1
      TCS=SUMJA**2./B
      PCS=TCS/B
      PUNCH 42
      PUNCH 57,TCSM
      PUNCH 58,TCVD
      PUNCH 59,TCB
      PUNCH 52
      PUNCH 47,PCSM
      PUNCH 48,PCVD
      PUNCH 49,PCB
25    FORMAT(A3,F6.4,F8.2,F8.2,F6.4)
26    FORMAT(I3)
27    FORMAT(A3)
30    FORMAT(9X,52HCOMBINATION RULES FOR PSEUDO-CRITICAL TEMPERATURE
     AN, 110HD PRESSURE)
32    FORMAT(9X,30HGAS IDENTIFICATION MIXTURE NO-,A3/)
35    FORMAT(10X,4HCOMP,5X,3HMOL,4X,8HCRITICAL,5X,8HCRITICAL,4X,
     5HCRITI,13HCAL)
36    FORMAT(11X,2HNO,5X,4HFRAC,3X,10HPRESS PSIA,3X,10HTEMP DEG R,
     13X,11HCOMP FACTOR/)
37    FORMAT(10X,A3,F10.4,F10.2,F13.2,F13.4)
42    FORMAT(9X,36HPSEUDO-CRITICAL TEMPERATURES - DEG R/)
47    FORMAT(9X,43HEMPIRICAL STATISTICAL MECHANICS **********,F8.2)
```

COMPUTER PROGRAM NO. 3 -- Continued

```
48      FORMAT(9X,43HVAN DER WAAL-BERTHELOT(INT.VIRAL APPROACH)*,F8.2)
49      FORMAT(9X,43HBERTHELOT (VIRAL APPROACH) ***************,F8.2)
52      FORMAT(9X,32HPSEUDO-CRITICAL PRESSURES - PSIA/)
57      FORMAT(9X,43HEMPIRICAL STATISTICAL MECHANICS ***********,F8.2)
58      FORMAT(9X,43HVAN DER WAAL-BERTHELOT(INT.VIRAL APPROACH)*,F8.2)
59      FORMAT(9X,43HBERTHELOT (VIRAL APPROACH) ***************,F8.2)
        GO TO 2
        STOP
        END
```

COMPUTER PROGRAM NO. 4

```
*C        PUTTING DATA FOR SPLINE INPUT IN THE CORRECT FORM
*C        N=NUMBER OF PRESSURES FOR A GIVEN TR
*C        M=MIXTURE NUMBER
*1        READ100,M,TR,PC,N
*         PUNCH50,N
*         DO2I=1,N,1
*         READ200,P,Z
*         PR=P/PC
*         PUNCH300,TR,PR,Z
*2        CONTINUE
*         GO TO 1
*50       FORMAT(I3)
*100      FORMAT(I3,7X,F6.3,3X,F8.2,2X,I3)
*200      FORMAT(F8.2,2X,F7.4)
*300      FORMAT(F6.3,4X,F7.3,3X,F7.4)
*         END
```

COMPUTER PROGRAM NO. 5

```
*C      GENERAL SPLINE CURVE ROUTINE
*C      FOURTH PROGRAM IN THE COMPRESSIBILITY CHART SERIES
*C      MATRIX SOLVED BY ORDINARY GAUSSIAN ELIMINATION
*C      NOTE THAT THE SECOND DERIVATIVE AT THE END OF THE CURVE IS ZERO
*       DIMENSIONX(35),Y(35),AL(35),A(35,36),S(35),W(35),G(35)
*       PUNCH99
*       DO2I-1,35
*       DO2J=1,36
*2      A(I,J)=0.0
*1      READ33,SPK
*       READ10,N
*       PUNCH102,SPK
*       PUNCH100
*       PUNCH101
*       DO3I=1,N
*3      READ20,TR,X(I),Y(I)
*       YIP=(Y(1)-1.0)/X(1)
*       N1=N-1
*       DO4I=2,N
*4      AL(I)=X(I)-X(I-1)
*       A(1,1)=AL(2)/3.0
*       A(1,2)=AL(2)/6.0
*       A(1,N+1)=(Y(2)-Y(1))/AL(2)-YIP
*       A(N,N-1)=AL(N)/6.0
*       A(N,N)=AL(N)/3.0
*       DO5K=2,N1
*       A(K,K-1)=AL(K)/6.0
*       A(K,K)=(AL(K)+AL(K+1))/3.0
*       A(K,K+1)=AL(K+1)/6.0
*5      A(K,N+1)=(Y(K+1)-Y(K))/AL(K+1)-(Y(K)-Y(K-1))/AL(K)
*       W(1)=A(1,1)
*       G(1)=A(1,N+1)/W(1)
```

COMPUTER PROGRAM NO. 5 -- Continued

```
*          DO6I=2,N
*          W(I)=A(I,I)-A(I,I-1)*A(I-1,I)/W(I-1)
*6         G(I)=(A(I,N+1)-A(I,I-1)*G(I-1))/W(I)
*          S(N)=G(N)
*          DO7I=2,N
*          J=N+1-I
*7         S(J)=G(J)-S(J+1)*A(J,J+1)/W(J)
*          XX=0.25
*8         XX=XX+0.25
*          K=0
*          DO9I=1,N
*          K=K+1
*          IF(X(I)-XX)9,11,11
*9         CONTINUE
*          GO TO 1
*11        IF(K-1)12,8,12
*12        YY=S(K-1)*(X(K)-XX)**3/6.0/AL(K)
*          YY=YY+S(K)*(XX-X(K-1))**3/6.0/AL(K)
*          YY=YY+(Y(K)-S(K)*AL(K)/6.0)*(XX-X(K-1))
*          YY=YY+(Y(K-1)/AL(K)-AL(K)*S(K-1)/6.0)*(X(K)-XX)
*          YP=-S(K-1)*(X(K)-XX)**2/(2.0*AL(K))
*          YP=YP+S(K)*(XX-X(K-1))**2/(2.0*AL(K))
*          YP=YP+(Y(K)-Y(K-1))/AL(K)
*          YP=YP-((S(K)-S(K-1))*AL(K))/6.C
*          YPP=S(K-1)*(X(K)-XX)/AL(K)+(S(K)*(XX-X(K-1))/AL(K))
*          PUNCH30,TR,XX,YY,YP,YPP
*          GO TO 8
*10        FORMAT(I3)
*20        FORMAT(F6.3,4X,F7.3,3X,F7.4)
*30        FORMAT(4X,F6.3,4X,F7.3,4X,F7.4,4X,F9.4,4X,F9.4)
*33        FORMAT(A3)
*99        FORMAT(5X,19HSPLINE CURVE OUTPUT)
```

COMPUTER PROGRAM NO. 5 -- Continued

```
*100      FORMAT(5X,26HRED      RED      COMP)
*101      FORMAT(5X,52HTEMP     PRESS    FACTOR    DZ/DPR    DZ2/,
*102      FORMAT(5X,30HGAS MIXTURE IDENTIFICATION NO-,A3/)
*         STOP
*         END
```